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HYPOSULPHITE LIXIVIATION
THE CHLORINATION PROCESS
COPPER SMELTING AND REFINING
LEAD SMELTING AND REFINING
ZINC SMELTING AND REFINING
ELECTROMETALLURGY

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PREFACE

The International Library of Technology is the outgrowth of a large and increasing demand that has arisen for the Reference Libraries of the International Correspondence Schools on the part of those who are not students of the Schools. As the volumes composing this Library are all printed from the same plates used in printing the Reference Libraries above mentioned, a few words are necessary regarding the scope and purpose of the instruction imparted to the students of—and the class of students taught by—these Schools, in order to afford a clear understanding of their salient and unique features.

The only requirement for admission to any of the courses offered by the International Correspondence Schools is that the applicant shall be able to read the English language and to write it sufficiently well to make his written answers to the questions asked him intelligible. Each course is complete in itself, and no textbooks are required other than those prepared by the Schools for the particular course selected. The students themselves are from every class, trade, and profession and from every country; they are, almost without exception, busily engaged in some vocation, and can spare but little time for study, and that usually outside of their regular working hours. The information desired is such as can be immediately applied in practice, so that the student may be enabled to exchange his

present vocation for a more congenial one or to rise to a higher level in the one he now pursues. Furthermore, he wishes to obtain a good working knowledge of the subjects treated in the shortest time and in the most direct manner possible.

In meeting these requirements we have produced a set of books that in many respects, and particularly in the general plan followed, are absolutely unique. In the majority of subjects treated the knowledge of mathematics required is limited to the simplest principles of arithmetic and mensuration, and in no case is any greater knowledge of mathematics needed than the simplest elementary principles of algebra, geometry, and trigonometry, with a thorough, practical acquaintance with the use of the logarithmic table. To effect this result, derivations of rules and formulas are omitted, but thorough and complete instructions are given regarding how, when, and under what circumstances any particular rule, formula, or process should be applied; and whenever possible one or more examples, such as would be likely to arise in actual practice—together with their solutions—are given to illustrate and explain its application.

In preparing these textbooks, it has been our constant endeavor to view the matter from the student's standpoint, and to try and anticipate everything that would cause him trouble. The utmost pains have been taken to avoid and correct any and all ambiguous expressions—both those due to faulty rhetoric and those due to insufficiency of statement or explanation. As the best way to make a statement, explanation, or description clear is to give a picture or a diagram in connection with it, illustrations have been used almost without limit. The illustrations have in all cases been adapted to the requirements of the text, and projections and sections or outline, partially shaded, or full-shaded perspectives have been used, according to which will best produce the desired results. Half-tones have been used rather sparingly, except in those cases where the general effect is desired rather than the actual details.

It is obvious that books prepared along the lines mentioned must not only be clear and concise beyond anything heretofore attempted, but they must also possess unequaled value for reference purposes. They not only give the maximum of information in a minimum space, but this information is so ingeniously arranged and correlated, and the indexes are so full and complete, that it can at once be made available to the reader. The numerous examples and explanatory remarks, together with the absence of long demonstrations and abstruse mathematical calculations, are of great assistance in helping one to select the proper formula, method, or process and in teaching him how and when it should be used.

The numerous questions and examples, with their answers and solutions, which have been placed at the end of each volume, will prove of great assistance to all who consult the Library.

Two of the volumes of this library, of which this is the second, deal with the metallurgy of gold, silver, copper, lead, and zinc. In the present volume the following subjects are treated: Hyposulphite lixiviation, the chlorination process, copper smelting and refining, lead smelting and refining, zinc smelting and refining, and electrometallurgy. Hyposulphite Lixiviation treats of the recovery of silver. The Chlorination Process treats of the recovery of gold. Copper Smelting, Lead Smelting, and Zinc Smelting all include the treatment of by-products. The papers entitled Electrometallurgy treat on the separation and recovery of different metals by electrolysis. In preparing this and the preceding volume on this subject, the aim has been to produce a work that would be of use to the practical mill man and metallurgist and also to the theoretical chemist. The practical working of the different processes is described in such a manner that those who are now engaged at metallurgical plants or who wish to become familiar with the processes in use there can obtain a thorough knowledge of them without consulting other authorities.

The method of numbering the pages, cuts, articles, etc. is such that each subject or part, when the subject is divided into two or more parts, is complete in itself; hence, in order to make the index intelligible, it was necessary to give each subject or part a number. This number is placed at the top of each page, on the headline, opposite the page number; and to distinguish it from the page number it is preceded by the printer's section mark (§). Consequently, a reference such as § 16, page 26, will be readily found by looking along the inside edges of the headlines until § 16 is found, and then through § 16 until page 26 is found.

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HYPOSULPHITE LIXIVIATION

LEACHING SILVER ORES WITH HYPOSULPHITE SOLUTIONS

HISTORY OF THE LIXIVIATING PROCESSES

1. Early attempts to lixiviate silver ores disclosed the necessity of first converting the silver into chloride, as neither the metal silver nor its compounds other than the chloride were more than slightly soluble in hyposulphite solutions alone.

To convert various ores of silver into chlorides, a chloridizing* roast was tried, but it was found to be impossible to conduct such a roast and convert all the silver into the chloride without a loss. The **Russell** process, therefore, was proposed, in order to treat compounds of silver other than the chloride, which it does to a certain extent, by first roasting to partially remove sulphur. Some silver ores that are oxidized can be treated directly without recourse to roasting or chloridizing roasting, nature having performed the preliminary operation for successful leaching. Lead that is dissolved during silver lixiviation can be precipitated from the solution as lead carbonate without the loss of other

* Chloridizing roasting consists in roasting ore with sodium chloride, $NaCl$.

metals, thus giving the silver precipitates a fair degree of fineness and eventually a finer bullion.

2. There are two silver lixiviating processes of interest to the metallurgist, which will be described: (1) *the von Patera process;* (2) *the Russell process.*

LABORATORY TESTS

3. Before describing these processes, the method of testing ores to ascertain if they may be leached by hyposulphite solutions will be discussed. The following points can be determined in the laboratory:

Whether the ore can be lixiviated raw or requires roasting.

The size of grains for the best lixiviation.

The percentage of salt for chloridizing roasting.

The loss of silver from volatilization.

The quantity of base metals dissolved by hyposulphite solutions.

Ores requiring roasting cause more work.

Roasting tests can be carried out in the muffle of an assayer's cupelling furnace in lots of about 3½ A. T. To accomplish this, use a clay dish 4½ inches in diameter, crush the ore to pass a 40-mesh screen, and mix with 10 per cent. by weight of salt. Desulphurizing should be done slowly and at a low heat under constant stirring. The temperature is raised as soon as the glowing particles cease to appear and the ore commences to swell, and then the charge is raised to a dull-red heat. Another similar charge is roasted longer and both are assayed for silver to ascertain the loss in roasting.

4. Action of Hyposulphite Solution on Silver.—To ascertain to what extent silver in an ore is attacked by hyposulphite solutions, $Na_2S_2O_3 + H_2O$, take 500 grams of ore and place it on a filter cloth *a* in a funnel *b* or some such arrangement as that shown in Fig. 1. Upon this ore a solution containing 2 per cent. sodium hyposulphite is poured and

allow to percolate through the ore into the beaker *d*. To find out whether the solution is dissolving silver, a few drops of a solution of sodium sulphide, Na_2S, are added to the liquor in the beaker, and if there is a black precipitate of silver sulphide, Ag_2S, the presence of silver is shown. In case there is no black precipitate formed by sodium sulphide, a few drops of a solution containing silver is added, to ascertain whether there is an excess of sodium sulphide in the beaker.

If an excess of sodium sulphide had been added, as will be shown by a black precipitate formed by the silver solution, it is taken for granted that the solution first tested contains no silver. Leaching is therefore stopped and the hyposulphite washed out with cold water, the deduction being that the ore is not suitable to hyposulphite leaching or contains no silver.

FIG. 1

5. Sodium-Sulphide Test.—Should the presence of silver be determined in the beaker as the solution comes from the ore, percolation is continued until no more silver is dissolved. To ascertain whether all the silver is dissolved from the ore, a little of the solution coming from the funnel is taken from time to time and tested with sodium-sulphide solution, until no further precipitate is given, when the leaching may be considered complete. No definite time can be given in which to complete the testing, as that is dependent on the ore and its previous preparation; however, as a usual thing, the test will occupy about twenty minutes.

6. The probable reaction that occurs when silver chloride is dissolved in sodium hyposulphite is expressed as follows:

$$2AgCl + 2Na_2S_2O_3 = Ag_2S_2O_3, Na_2S_2O_3 + 2NaCl$$

The reaction that occurs when sodium sulphide is added to the double silver-hyposulphite salt is

$$Ag_2S_2O_3, Na_2S_2O_3 + Na_2S = Ag_2S + 2N_2S_2O_3$$

The ore, before the lixiviating test is made, should be assayed to ascertain the quantity of silver it contains. The leached ore is washed, dried, and then assayed for silver, to ascertain the quantity of silver dissolved by the sodium-hyposulphite solution. The difference between the two assays should show the quantity of silver extracted by the sodium-hyposulphite solution. It will be noticed that in the reaction which precipitates silver sulphide, sodium hyposulphite is regenerated.

7. To Determine the Percentage of Sodium Hyposulphite in a Solution.—Free iodine when brought in contact with sodium-hyposulphite solution changes the latter into sodium iodide, according to the formula

$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI$$

Free iodine added to a solution containing starch produces a blue color, and advantage is taken of this fact to determine the percentage of hyposulphite in a solution. If a small quantity of starch is added to a hyposulphite solution and a solution of iodine is added drop by drop, the blue color produced by iodine and starch is destroyed as soon as formed so long as hyposulphite exists in the solution. The moment all the hyposulphite is changed, as indicated by the above reaction, the least excess of iodine will form a permanent blue color with starch.

8. Preparation of a Standard Iodine Solution.—To make a standard iodine solution for testing hyposulphite solutions, 5.11 grams of iodine are placed in a small beaker, 6 grams of potassium iodide are added, and then about 15 c. c. of water. In about 20 minutes the iodine will be dissolved, after which 200 c. c. of water are added and the clear liquid decanted off. If any iodine remains undissolved, 3 or 4 grams of potassium iodide are added to it. Usually this second

addition of potassium iodide is sufficient to dissolve all the iodine, but if not, the same operation is repeated until all iodine is dissolved. The whole solution is then diluted with cold water to 1,000 c. c. and placed in a glass-stoppered bottle. One gram of pure hyposulphite of soda should correspond to 100 c. c. of this solution.

9. To prepare the starch solution for titration, take about 10 grams of starch and boil in from 500 to 1,000 c. c. of water. Saturate the starch solution with salt and allow it to stand until clear, then decant off. The salt is added to prevent the starch solution souring, but even then it should be made fresh every two or three days.

10. To Test the Solution.—To make a test of a hyposulphite solution, measure out 10 c. c. with the pipette and place in a beaker. Add to this a few drops of the starch solution. Run into this mixture the standard iodide solution from a burette previously filled. When a permanent faint-blue color is perceptible, the titration is completed. Each cubic centimeter of iodine solution corresponds to one-tenth of 1 per cent. of hyposulphite of soda.

LEACHING TESTS FOR THE RUSSELL PROCESS

11. In the following tests the quantity of ore used is 14.583 grams, or ½ A. T.

The ore tested is to be assayed before and after leaching for silver, the difference in the assays showing the quantity extracted by lixiviation. What is known as the extra solution is cuprous hyposulphite. The copper solution of the tests is made by dissolving 200 grams of copper sulphate, $CuSO_4$, in hot water and then diluting the solution to 1,000 c. c., which makes it a 20-per-cent. solution. When treating roasted or chloridized ores, a preliminary water washing is given them, for the purpose of removing base-metal salts prior to the extraction of silver; this prevents the fouling of leaching solutions and assists in the work. But in the

laboratory, leaching tests are made with and without preliminary washing, to ascertain the solubility of the principal salts that are encountered in base-metal leaching.

12. To Test Raw and Roasted Ores.—Different tests are required for roasted and raw ores. Thêse are given after the grouping of Russell and Stetefeldt as far as possible.

The ½ A. T. of ore is placed in beakers having 300 c. c., and the contents of the beaker is occasionally stirred. Hyposulphite solution is made from 250 c. c. of water and 20 grams of hyposulphite. The ore is allowed to remain in contact with this solution. When either wash water or hyposulphite solution is used on the ore, it is decanted upon a filter that is used to receive the ore in the final washing. After final washing, the filter and ore are transferred to a flat dish and dried. When dry, the filter is removed, burned, and returned to the ore, which is then ready for assay.

If the fire assay is made by scorification assay, the presence of filter-paper ash is inconvenient, and in such cases the last traces of the ore are removed from the dry filter with a stiff brush and the paper thrown away.

LIXIVIATING ROASTED ORES

WASH WATER OMITTED; COPPER SOLUTION IS ADDED FIRST

13. Solutions Not Heated; Time of Exposure Short. To ½ A. T. ore add 50 c. c. cold water and 25 c. c. $CuSO_4$; let stand 2 hours; dilute to 300 c. c. with cold water, add 20 grams hyposulphite sodium, $Na_2S_2O_3$; let stand 2 hours; filter and wash. Assay the tailings.

This test may be reversed by adding the bulk of the water to the ore first and after standing 2 hours adding the hyposulphite.

14. Solutions Not Heated; Exposure Long.—To ½ A. T. ore add 250 c. c. cold water and 25 c. c. $CuSO_4$ solution; let stand 12 to 18 hours; then add 20 grams $Na_2S_2O_3$ and let stand 12 to 18 hours longer before filtering and washing. Assay tailings as before.

15. Solutions Heated; Exposure Short.—Add to ½ A. T. ore 250 c. c. cold water and 25 c. c. $CuSO_4$ solution and let stand 1 hour, cold. Add next 20 grams $Na_2S_2O_3$; heat to 131° F.; decant. Add to same ore 250 c. c. cold water and 25 c. c. $CuSO_4$ solution; let stand 1 hour. Next, add 20 grams $Na_2S_2O_3$; heat to 131° F.; filter and wash. Assay tailings as directed.

ORE IS FIRST LEACHED WITH WATER

16. Solutions Used Cold; Copper Added First; Time of Exposure Long.—Leach ½ A. T. roasted ore with cold water; add 25 c. c. $CuSO_4$; dilute to 300 c. c. with cold water and allow the mixture to stand from 12 to 18 hours; then add 20 grams $Na_2S_2O_3$; let the mixture stand 12 to 18 hours, cold; filter and wash the ore on filter with hot $Na_2S_2O_3$ solution. Assay tailings as directed.

17. Solutions Heated; Time of Exposure Short.—(*a*) Leach ½ A. T. of roasted ore with hot water; after draining, add 200 c. c. hot water and 90 c. c. $CuSO_4$ solution; let stand ½ hour before adding 90 grams $Na_2S_2O_3$. Heat the solution obtained to 149° F.; filter and wash.

(*b*) Leach ½ A. T. ore with hot water; add 90 c. c. $CuSO_4$; let stand ½ hour; then add 90 grams $N_2S_2O_3$ and dilute to 300 c. c.; heat to 149° F. Filter and wash.

18. Hyposulphite Added First.—Leach with hot water; add 20 grams $Na_2S_2O_3$; let stand with 30 to 40 c. c. water 1 hour; add 25 c. c. $CuSO_4$; dilute to 300 c. c. with cold water; heat to 131° F.; filter and wash. Dry the tailings as directed and assay.

LIXIVIATING RAW ORES

19. Solutions Used Cold; Time of Exposure Long.—Take ½ A. T. raw ore, add 250 c. c. cold water and 20 grams $Na_2S_2O_3$; let stand in a beaker 12 to 18 hours; decant; add 25 c. c. $CuSO_4$ solution; dilute with 300 c. c. cold water and let stand another 12 to 18 hours. Add next 20 grams $Na_2S_2O_3$; let stand 12 to 18 hours; filter and wash. Assay tailings as directed.

20. To ½ A. T. raw ore add 250 c. c. cold water and 20 grams $Na_2S_2O_3$; let these remain in contact 12 to 18 hours; then add 20 grams $CuSO_4$ solution and 20 grams $Na_2S_2O_3$; let stand 12 to 16 hours, cold; filter and wash. Assay tailings as directed.

21. To ½ A. T. raw ore add 100 c. c. cold water and 25 c. c. $CuSO_4$ solution; let stand 12 to 16 hours, cold; dilute to 300 c. c. with cold water; add 20 grams $Na_2S_2O_3$; let stand 12 to 16 hours, cold; filter and wash on filter with hot $Na_2S_2O_3$ solution.

22. Solutions Heated; Time of Exposure Short.—To ½ A. T. raw ore add 100 c. c. cold water and 25 c. c. $CuSO_4$ solution; let stand 1 hour; next add 200 c. c. cold water and 20 grams $Na_2S_2O_3$; heat to 131° F.; filter and wash. Assay tailings.

23. To ½ A. T. raw ore add 250 c. c. cold water and 25 c. c. $CuSO_4$; let stand 1 hour, cold; add 20 grams $Na_2S_2O_3$; heat to 131° F.; decant; add 100 c. c. cold water and 25 c. c. $CuSO_4$ solution; let stand 1 hour, cold; add 20 grams $Na_2S_2O_3$; heat, filter, and wash.

24. To the same quantity of ore as before add 200 c. c. cold water and 90 c. c. $CuSO_4$ solution; let stand 1 hour; add 90 grams $N_2S_2O_3$; heat to 149° F.; filter and wash. Assay tailings.

25. Add 250 c. c. cold water and 25 c. c. $CuSO_4$ solution to ½ A. T. raw ore and heat the mixture to 131° F.; decant; add 20 grams $Na_2S_2O_3$, 25 c. c. $CuSO_4$ solution, and

300 c. c. cold water; heat to 131° F.; filter and wash. Assay tailings.

26. To $\frac{1}{2}$ A. T. raw ore add 200 c. c. hot water and 90 c. c. $CuSO_4$ solution; let stand $\frac{1}{2}$ hour. Next add 90 grams $Na_2S_2O_3$; heat to 149° F.; filter and wash.

27. The Necessity for Tests.—The various methods of testing described are more essential probably for lixiviation by hyposulphite solutions than for other lixiviation or even amalgamation. Sometimes the extraction by chlorination and amalgamation tests closely corresponds; at other times no such agreement exists.

An ore may, owing to the presence of silver antimonate and arsenate, give a high chlorination test, while its values cannot be extracted well by amalgamation.

28. It often occurs, on the other hand, that amalgamation gives a higher silver yield than the chlorination tests, and then silver remains in the tailings that can be extracted by lixiviation. In this case the difference may be due to metallic silver and possibly other causes, the nature of which are unknown.

VON PATERA PROCESS

29. Introduction.—The extraction of silver by sodium hyposulphite was introduced by von Patera, an Austrian, in 1858. It depends on the fact that silver chloride is soluble in hyposulphite solutions. In 1860, Kiss substituted calcium hyposulphite for sodium, since which time the process has been indiscriminately known by either of the originator's names or simply as hyposulphite lixiviation. The **von Patera** process can be used where the ore does not contain much base metal; for instance, if the ore contains lead sulphate, it also will be dissolved. If copper is present in the roasted ore as cuprous chloride, the sulphides precipitated from the hyposulphite solution will contain silver, copper, and lead. Ores that contain appreciable quantities of

gold, so as to make it worth while, may be first leached by sodium-hyposulphite solutions and afterwards have their tailings treated by the chlorination process for gold. When calcium hyposulphite is the leaching solution, the silver and gold can be recovered together.

30. Method of Procedure.—The von Patera process, which in our description also includes the **Kiss**, requires skilful manipulation and close watching during its various stages, for if neglected in any one stage, serious losses are likely to occur.

This process consists of the following steps:

1. Crushing the ore, since in this state it is easier to dry, roast, and lixiviate.
2. Drying the ore, to expel moisture.
3. Roasting the ore with salt, to form metal chlorides.
4. Leaching out the base metals with water, to obtain purer bullion and save chemicals.
5. Leaching with hyposulphite of soda, to extract silver.
6. Precipitating the silver as a sulphide.
7. Roasting the sulphide of silver and melting the bullion.

31. Salt for Chloridizing Roast.—For the chloridizing roast, about 80 pounds of sodium chloride are mixed with 2,000 pounds of ore before the ore is introduced into the roasting furnace. Experience has shown that less salt is required for chloridizing if it is mixed with the ore in the driers. The ore is roasted with great care, if base metals are present which it is desirable to save. If lead is present, roasting must be done at a low temperature, as the compounds of lead are easily fusible and might agglomerate; or if silica is present, lead silicate might be formed, which would prevent contact of the leaching solution with some of the silver. The temperature of the roaster must be just right for converting the lead into chloride, as this is soluble in hot water, while the sulphate of lead is not.

After the ore has roasted about 7 hours it is discharged into pits, where it cools in a few hours, so that it can be

removed in cars to the cooling floor. The trained eye will recognize when the ore is sufficiently roasted by its sluggish motion in the furnace. When the ore is discharged into the pits, assay samples are taken to determine the amount of silver in the ore, also for the chlorination test, which is made for each charge. After reaching the cooling floor, the roasted ore is moistened with water to keep the dust down.

METHOD OF LEACHING

32. Hyposulphite Leaching Vats.—For the purpose of **leaching**, ore is removed from the cooling floor by proper appliances and placed in *leaching vats*. These vats are similar in most respects to cyanide vats, especially their false bottoms and leaching devices, and as they have been described, it is not necessary to repeat their detailed construction here.

The vats are made large in diameter: 7 feet deep if the tailings are to be sluiced out and 5 feet deep if the tailings are to be shoveled out. The details of a hyposulphite leaching plant are given in Fig. 2, and will be referred to in the text from time to time as the different operations are touched on.

33. Base-Metal Leaching.—Silver lixiviation by hyposulphite solutions involves two distinct operations, one for base-metal chlorides and the other for silver chlorides. In the first instance the ore is leached with water, and in the second with hyposulphite solution, to extract the silver.

Assuming that hot water is used for leaching base-metal chlorides, it will be introduced first through the bottom of the vat until the ore is submerged. It is well to know that the vats are not to be filled to the top with ore and that it is customary in practice to leave from 9 to 12 inches between the ore and the top of the vat. This method of wetting the ore is quicker and more uniform than where the solution is run on dry ore from the top. After the ore has been submerged a few minutes, the discharge pipe is opened and

the water allowed to percolate into the launder *d*, Fig. 2. While the water is draining from the bottom, a further

FIG. 2

supply of wash water is being added to the top of the vat. After a time the wash water coming from the bottom of the

vat is tested with sodium sulphide, and when it shows no precipitate of the base metals, the washing is stopped.

34. Percolation Methods.—When the water introduced from the bottom subsides, a *thin crust* is left on top of the ore, which is very *rich in silver*. It contains the silver that was dissolved by the excess of salt or other chlorides in the ore and is precipitated by dilution with water. This would have been lost if hot water had been added to the top of the leaching vat at first.

When the ore contains an excess of lead or antimony, the percolation must be from the top, as the chlorides of these metals are precipitated from the solution by dilution with water. The solution is passed through precipitating boxes containing wood shavings. A stream of water is allowed to flow into these shavings with the solution from the tanks, and by the dilution of this solution the silver, lead, and antimony chlorides are deposited on the shavings. These metals can be dissolved from the shavings by using a solution of sodium hyposulphite. The wash water will remove sodium chloride and sulphates of the base metals, such as the sulphates or chlorides of aluminum, calcium, iron, manganese, zinc, or copper. The cold water is allowed to run on to the ore as fast as it drains from below the ore. When leaching with water is completed, the water is drained off. When drainage is stopped, the hyposulphite solution is turned on.

35. Silver Leaching.—After removing the base-metal salts, the extraction of silver chloride is undertaken by leaching with hyposulphite solutions of a proper strength. The strength of the silver leaching solution will depend on the richness of the ore and the quantity of base metals present. With the majority of ores a 1-per-cent. solution will answer, but with rich ores solutions containing up to 2 per cent. of hyposulphites can be employed; however, with the richest ores, the solutions should not exceed the latter figure in strength.

The hyposulphite solution is run on from the top of the vat and is allowed to pass through the vat so long as any

silver is dissolved. The reaction that occurs is expressed by the following equation:

$$2AgCl + 2Na_2S_2O_3 = 2NaCl + Na_2S_2O_3 \cdot Ag_2S_2O_3$$

The sodium-silver hyposulphite formed (which is soluble in water) is drained into the silver precipitating tanks *f*, Fig. 2. The time consumed in treatment is usually less than 30 hours; however, it depends to a great extent on the richness of the ore, rich ores requiring a longer time.

36. Washing the Tailings.—As soon as the hyposulphite solution has subsided by drainage to the surface of the ore, cold water is turned on at the top of the tank. When the tank is full the water is turned off, and when the water subsides to the surface of the tailings the discharge water is turned into the fresh-water tank or is let run to waste. A tank can be charged with ore, leached, and the tailings discharged in less than 48 hours.

Average samples of tailings should be taken from each leaching vat and assayed before it is discharged, so as to know the percentage of extraction that has taken place. When an ore assays 30 to 50 ounces before leaching, the tailings should not assay above 4 ounces of silver to the ton.

PRECIPITATION OF THE SILVER

37. Handling the Solution.—The hyposulphite solution containing the silver, as before stated, is run directly from the leaching vats *b*, Fig. 2, into the precipitating tanks *f*. The precipitating tanks are usually 8 feet in diameter and 12 feet deep. When it is possible, these tanks should be placed 3 feet below the bottom of the lixiviation tanks, in order to take advantage of gravity. When all the tanks are placed on the same level, the solution is pumped into the precipitating tanks from the leaching vats. The solutions are conducted through the mill in iron pipes carefully coated on the inside with an asphalt paint.

38. Precipitating With Calcium Sulphide.—The precipitating tank is filled to within 20 inches of the top with the silver solution, and then calcium sulphide is added to precipitate the silver, the solution being agitated during the addition of the precipitant. The following equation represents the reaction:

$$Ag_2S_2O_3 \cdot Na_2S_2O_3 + CaS_2 = Ag_2S + Na_2S_2O_3 \cdot CaS_2O_3 + S$$

When the precipitate subsides, the clear solution is drawn off into a sump tank *k*, shown in Fig. 2, which is, if possible, on a *lower* level than the precipitating tank. The solution is next pumped from the sump tank *k* to the storage tank *a*, which is, if possible, on a *higher* level than the leaching vats.

39. There should not be an excess of calcium sulphide used, as only that part of the calcium sulphide which precipitates the silver is converted into calcium hyposulphite. Any excess of sulphide would precipitate any silver contained in the hyposulphite solution of the storage tanks as an insoluble sulphide, which would be lost in the next leaching. If there is an excess of calcium sulphide, some of the solution containing silver must be added to neutralize it.

The precipitated silver sulphide is left in the bottom of the precipitating tanks until a number of precipitations have been made, then it is collected on filter *h*, shown in Fig. 2, and dried.

40. Collecting the Precipitate.—The clear solution in the precipitating vat is drawn off through the pipes *n*, shown in Fig. 2, into sump tank *k*. After the clear solution is removed, the discharge valve is closed. The sulphides on the bottom of the vat are stirred thoroughly and drawn off at the bottom of the tank through the stop-cock *i* into the filter *h*.

41. Description of the Filter.—The filter consists of a series of frames *h*, about 2½ feet square, over which sacking is spread. It is necessary to have a sufficient number

of these frames to take care of the precipitate. The solution from the precipitating tank is run on to these filters in such a way that the solution containing the sulphides flows from one to the other. The liquor passes through, while the sulphide precipitate remains on the sacking. This operation is repeated until the sulphide of silver has collected in considerable quantity on the sacking. The precipitate is then washed with clean water, to remove the excess of calcium sulphide. After drying, it is ready for roasting.

42. Roasting Silver-Sulphide Precipitates. — The silver having been thrown down as a sulphide, it becomes necessary to drive off the sulphur before melting down into bullion. For this purpose the dried precipitates are removed from filter and roasted in a small reverberatory furnace. At first the precipitates are kept at a low heat, in order to burn off a portion of the sulphur, after which the temperature is slowly increased until most of the remaining sulphur is driven off as gas. When this last stage is reached, the precipitates are heated as hot as possible without melting the silver. The product of the roast is a gray mass composed almost entirely of silver.

DESCRIPTION OF THE VON PATERA PROCESS PLANT

43. Location of Plant.—Leaching plants should be located, if possible, on a side hill, in order to take advantage of gravitation and thereby avoid considerable brine pumping. Such locations also avoid elevating ore and afford tailing dumps. If the solution vats are situated above the leaching vats, the solution will flow into the latter; similarly, the liquor will drain from the leaching vats into the precipitation vats and finally into the sump. If the vats are all on the same level, the brine must be pumped from one to the other, thus requiring four pumps where one would answer in the case of a side-hill location.

44. General Arrangement of Plant.—The general arrangement of an ordinary hyposulphite leaching plant is

shown in Fig. 2. The hyposulphite-of-sodium tanks *a* are elevated above the leaching vats *b*, the liquor flowing from the former to the latter through the pipe *c*. The leaching vats drain into a launder *d* that is divided into two compartments, one of which drains into the base-metal precipitating tank *e* and the other into the silver precipitating tank *f*. The discharge pipe *g* of the leaching vat is supplied with a valve, also a short rubber pipe, and when it is desired to discharge into either division of the launder, the rubber hose is placed in that division. The precipitating sulphide-of-calcium solution flows from the tank *l* into tanks *e* and *f* through the pipe *p*, as shown in the figure.

From the precipitating vats the liquor and precipitates are drained into the filter *h* through the pipes *i*. From the filter the liquor flows to the sump *k*, from which it is pumped to the hyposulphite-of-sodium tanks *a*, to be standardized. In order to save time, a portion of the clear liquor is decanted from the precipitating vats *f* to the sump tank *k*.

THE RUSSELL PROCESS

45. The Leaching Solution.—If ores containing much lead are treated with hyposulphite of calcium or sodium, a large proportion of the metal will be dissolved. If, at the same time, copper is present, the sulphides precipitated from the solution will contain silver, copper, and lead, a combination of metals not desirable for subsequent treatment.

The lead can be completely separated from sodium-hyposulphite solution, in the form of lead carbonate, by the addition of sodium carbonate, the reaction not precipitating any copper or silver. This method, however, prohibits the use of calcium polysulphide as a precipitant for the sulphides, because any calcium entering the regenerated lixiviation solution would also be precipitated as carbonate with lead by the sodium carbonate formed. Hence, a sodium sulphide must be employed.

46. Objections to Hyposulphite of Sodium.—Another defect in the hyposulphite-of-sodium and the hyposulphite-of-calcium lixiviation process consists in the necessity for a perfect chloridizing roast of silver in the ore, because silver in any other combination than silver chloride would be imperfectly extracted. In some instances the Russell process can be employed to extract silver from ores without roasting. Again, if silver chloride be treated with sodium hyposulphite and then with the Russell solution composed of **sodium-copper thiosulphate,** or **cupreous hyposulphate,** an additional quantity of silver is extracted, which would have been lost in the tailings by the old method.

47. The Precipitation of Lead.—The carbonate of lead, $PbCO_3$, is insoluble in a sodium-hyposulphite solution, while silver and copper carbonates are soluble. Hence, if carbonate of sodium is added to a hyposulphite solution containing lead, silver, and copper, lead alone is precipitated. If a solution of pure lead sulphate, $PbSO_4$, in sodium hyposulphite is so treated, the precipitation of lead carbonate is so complete that hydrogen sulphide, H_2S, gives no reaction in the filtrate. Upon the foregoing reactions is based the separation of lead from silver and copper in the Russell process.

48. Cuprous-Hyposulphite Solution.—In the Russell process, silver present in ore as simple sulphide, or in combination with arsenic and antimony sulphides, or as arsenate or antimoniate, as well as that present in the metallic state, together with gold, is dissolved by a solution of cuprous hyposulphite. After the above metals have been dissolved, the silver may be precipitated from the solution and the sulphide precipitate worked up for metallic silver.

49. The Extra Solution.—Cuprous hyposulphite is formed, according to Russell, about as follows:

$$13Na_2S_2O_3 + 6CuSO_4 = 4Na_2S_2O_3,\ 3Cu_2S_2O_3 + 6Na_2SO_4 + 3Na_2S_4O_6$$

The double salt $4Na_2S_2O_3$, $3Cu_2S_2O_3 + H_2O$ is known as sodium-copper thiosulphate, cuprous hyposulphite, and the **extra solution,** to distinguish it from the ordinary solution containing only sodium hyposulphite. The extra solution quickly decomposes silver sulphide, the silver going into solution and copper sulphide being produced. One part of the solid salt is capable of bringing .113 to .136 part of silver into solution. Solutions of the alkalies and alkaline chlorides do not attack silver sulphide, though cyanides do. This explains why the extra solution gives better results on ore containing base metals when there are no metals present to decompose the double salt.

50. Solubility of Silver Carbonates.—Lead can be precipitated by sodium carbonate from the leaching solution. Lead carbonate so found is almost insoluble in sodium-hyposulphite solutions, while the carbonates of silver and copper are very soluble. The carbonates of iron, manganese, zinc, and calcium are also insoluble in hyposulphite solutions. These salts do not get into the hyposulphite solution as they are removed by the wash water, because their salts are far more soluble in water than lead sulphate.

The following are some of the advantages of removing the lead by separate precipitation:

1. The silver-sulphide precipitate is practically free from lead, thus saving expense in refining.

2. The lead is obtained in a clean, compact form, free from copper, iron, zinc, etc.

3. Absence of lead sulphate in the hot-stock solution.

4. Saving of sodium sulphide.

CHART OF RUSSELL PROCESS

51. Ore Suitable for the Process.—The following chart, Fig. 3, shows the scheme of the operation. It may be as well to mention here that tailings from the Patio, Washoe, and von Patera processes may sometimes be treated successfully by the extra solution.

The *first operation* for the Russell process is the preparation of the material for lixiviation. If the material be

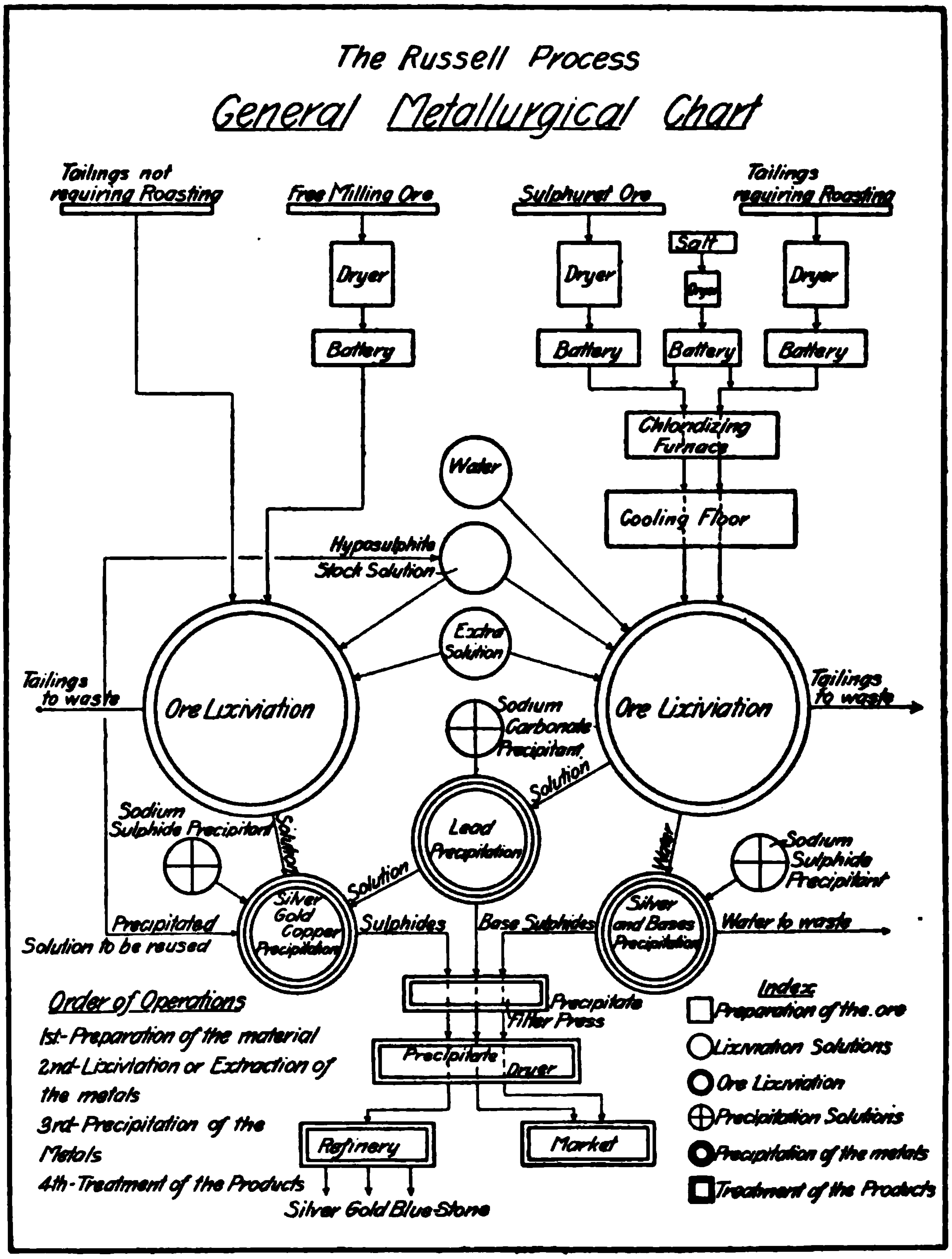


FIG. 8

tailings from other processes, they may or may not require roasting; if not, they are placed directly in the lixiviation

tank. Tailings requiring a chloridizing roast are first dried to remove the moisture; they are next screened to break up any lumps and to size them for the furnace; they are then placed in the furnace and roasted, salt being added to form chloride of silver. The tailings are removed from the furnace to the cooling floor and from there to the lixiviating vat.

52. Treatment for Free Milling Ore.—Free milling ore, if lixiviated, is dried to remove moisture and then run through the stamp mill and over the battery plates. Such portion of the ore as escapes from the amalgam on the battery plates is placed in the lixiviation vat for treatment, first with sodium or calcium hyposulphite and afterwards with the extra solution.

53. Treatment of Sulphides.—Ore containing sulphides is dried, then crushed and given a chloridizing roast. From the furnace it is removed to the cooling floor, where chloridizing continues until the ore is cool. In some cases it may be desirable to more thoroughly mix salt with ore or tailings than can be done in the furnace. If such be the case, the salt is mixed with the ore before being placed into the drier, for salt carries considerable water of crystallization and would not stamp dry, but form a paste at the battery. Chloridizing, cooling, and lixiviation follow stamping.

54. Lixiviation.—The *second operation*, as shown in Fig. 3, is that of lixiviating the ore. The hyposulphite-solution and the extra-solution tanks have connection with the lixiviation vats and supply whatever quantity of solution is necessary for the ore treatment. From the lixiviating vats, the liquor now containing metals in solution is drained into the precipitating tanks. It will be noticed that base-metal solutions are drained into the lead precipitation tank, after which the ore is washed with water and the drainage carried into the silver and base-metal precipitation tank.

55. Precipitating the Metals.—The *third operation* is the precipitation of the metals from the solution. The lead is precipitated in the lead precipitation tank by a solution of sodium carbonate. The remaining solution is run to the

copper, gold, silver tank, and after these metals are precipitated by sodium sulphide, the remaining liquor is pumped back to the hyposulphite stock-solution tank. The silver and bases from the base metal ores are precipitated by a sodium-sulphide solution.

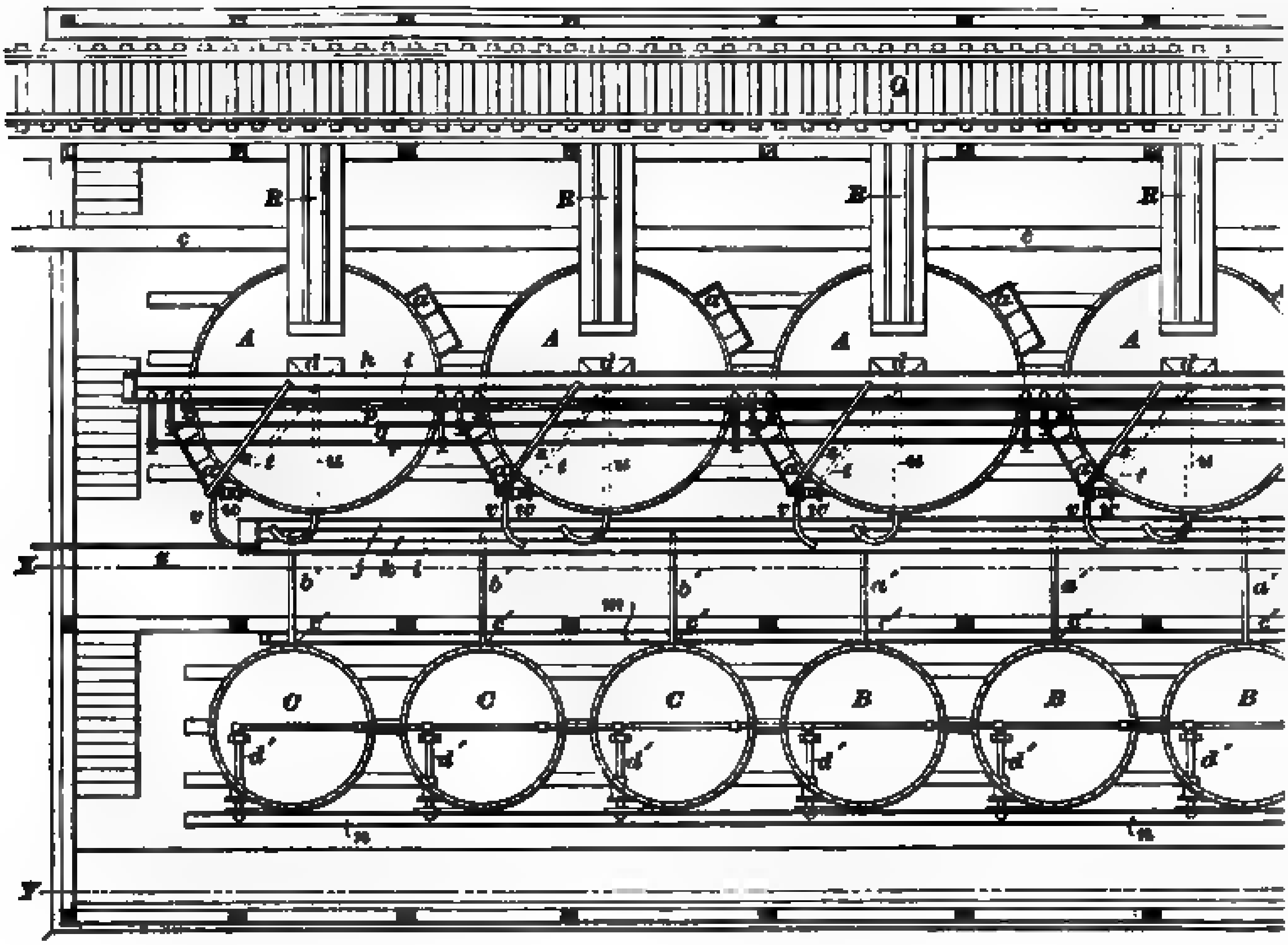
56. Collecting the Precipitates.—The *fourth operation* is collecting the sulphides and running them through the filter press and drier. The silver, gold, and copper are refined. The base sulphides are sent to market to be refined. The lead-carbonate precipitate is dried and sent to market. The base sulphides are not easily refined and it is usually considered much cheaper to ship them away to metallurgical works that make a business of refining.

DESIGN OF A RUSSELL PLANT

57. The working drawings shown by Figs. 4 and 5 are from notes on the Russell process by Mr. Daggett. These working drawings comprise the best features of the plants that have been constructed and operated by the originators of the Russell process. The plant may be located in any convenient place, so as to secure the most economical transportation of the ore to it and the leached tailings from it.

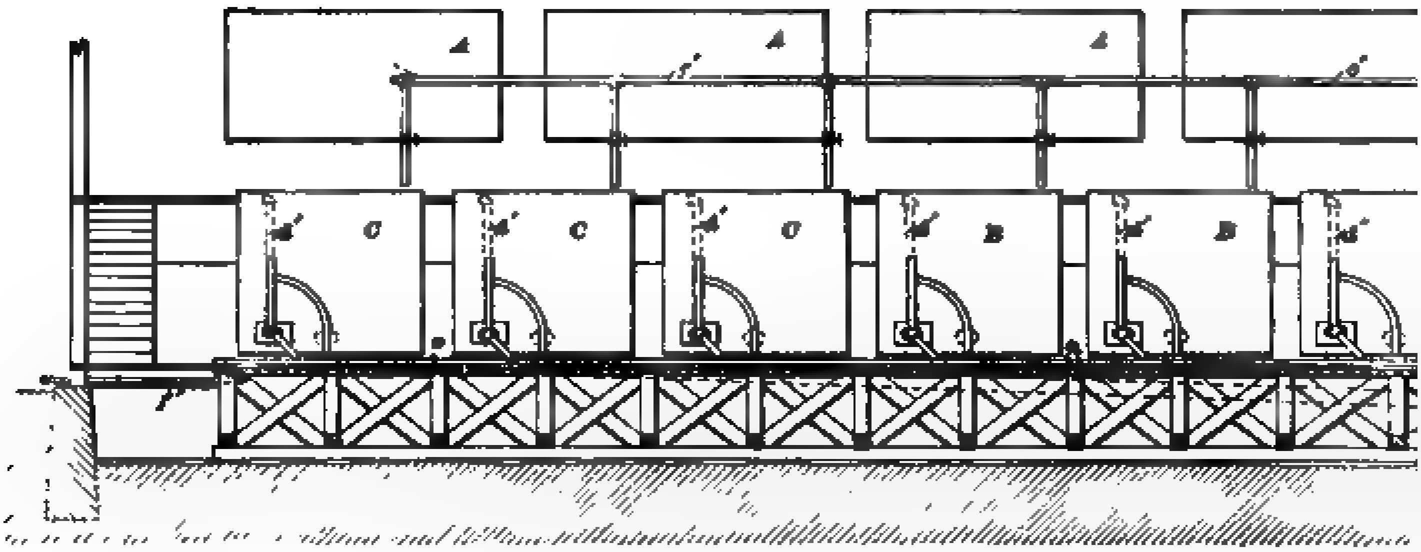
The following is an index to the parts of the plant, shown in Figs. 4 and 5. It will be noted that the process requires considerable apparatus, none of which, however, is very intricate or requires extra-skilled labor. The process itself requires careful manipulation or oversight by experienced men, while the actual labor can be performed by ordinary men. All letters refer to the ground plan, Fig. 4 (*a*), unless otherwise stated.

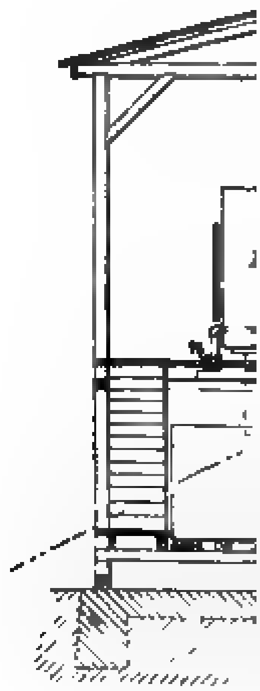
A, leaching tanks; *B*, solution precipitating tank; *C*, wash-water tanks; *D*, solution pump-sump tank; *E*, storage tank for sulphides; *F*, filter-press sump; *G*, storage tanks for solution; *H*, storage tank for hot solution or for preparation of extra solution; *I*, cast-iron tank for preparation of sodium sulphide; *J*, sheet-iron tanks for storing sodium sulphide; *K*, iron pressure tank; *L*, filter press for sulphides;



(a)

Fig. 4.





M, steam drier for sulphides; *N*, boiler; *O*, fire pump for sluicing; *P*, solution pump; *Q*, main ore track to leaching tanks; *R*, side tracks to leaching tanks; *S*, side tracks in chemical room; *T*, grade line between boiler and steam drier, Fig. 5 (*b*); *U*, grade line through sulphide storage tank, Fig. 5 (*c*).

a, tailing chute (to cars); *b*, sluice gate for tailings, Fig. 5 (*c*); *c*, sluice trough for tailings; *d*, box for chemicals for extra solution, Fig. 5 (*c*); *e*, ore car; *f*, ore-car truck; *g*, chemical car; *h*, special extra trough over leaching tanks; *i*, solution trough over leaching tanks; *j*, solution trough to solution precipitating tanks; *k*, wash-water trough to wash-water precipitating tanks; *l*, waste-water trough; *m*, trough to conduct sulphides to sulphide storage tank; *n*, trough to conduct solution to solution-pump sump; *o*, waste wash-water trough, Fig. 5 (*a*); *p*, solution pipe to leaching tanks; *q*, hot-solution or extra-solution pipe to leaching tanks; *r*, water pipe to leaching tanks; *s*, hose for circulating extra solution; *t*, hose from leaching tank to siphon pump; *u*, hose from leaching tank to triple launder; *v*, hose from siphon pump to triple launder; *w*, siphon pump; *x*, tailing car, Fig. 5 (*c*); *y*, hose connections for sluicing, Fig. 4 (*b*); *z*, waste-water pipe from triple launder.

a', pipes from triple launder to solution precipitating tanks, Fig. 5 (*c*); *b'*, pipes from triple launder to wash-water precipitating tanks; *c'*, valve, or gate, for sulphides; *d'*, surface discharge for precipitating tanks; *e'*, sodium-sulphide pipe, Fig. 5 (*a*) and (*c*); *f'*, pipe for precipitated wash water, Fig. 5 (*a*); *g'*, connection between solution pump and sump, Fig. 5 (*a*); *i'*, drip pipe from solution pump, Fig. 5 (*b*); *j'*, pipe from pump to storage tanks, Fig. 5 (*a*) ; *k'*, connection between sulphide storage tank and pressure tank, Fig. 5 (*a*); *l'*, connection between pressure tank and press; *m'*, siphon pump in filter-press sump, Fig. 5 (*a*); *n'*, pipe for returning solution to solution sump, Fig. 5 (*a*); *o'*, small windlass for steam drier, Fig. 5 (*a*); *p'*, boxes over storage tanks, to prevent agitation of the solution, Fig. 5 (*b*); *q'*, boxes and strainers around outlets, Fig. 5 (*a*); *r'*, lead

heating coils in storage tanks, Figs. 4 (*a*) and 5 (*b*); *s'*, drip from lead coils, Fig. 4 (*b*); *t'*, triple connection between the three storage tanks; *u'*, main steam pipe, Fig. 4 (*b*); *v'*, water pipe from fire pump for sluicing, Fig. 4 (*b*); *w'*, storage room for caustic soda and sulphur, Fig. 4 (*b*); *x'*, storage room for bluestone and hyposulphite, Fig. 4 (*b*); *y'*, trap door to filter-press sump; *z'*, gauge valve on side of pressure tank, Fig. 5 (*a*).

a'', solution pipe to sodium-sulphide storage tanks, Fig. 5 (*a*); *b''*, pipe for drawing off sediment from pump sump, Fig. 5 (*a*); *c''*, pipe for drawing off sediment from solution storage tanks, Fig. 5 (*b*); *d''*, siphon pump for circulating solution through chemical box in extra-solution tank, Fig. 5 (*b*).

DETAILS OF CONSTRUCTION

58. Lixiviation Tanks.—These are usually made of white cedar or cypress. The dimensions are given in the working drawings, Fig. 6 (*a*) and (*b*). The staves and bottoms are 3 inches thick. C. A. Stetefeldt gives the following directions for making a vat: "The staves should be cut to the sweep of vat and 9 inches longer than the inside height, but not gained for the bottom, and the latter should be without dowel-pins and cut to a diameter 2 inches greater than that of the finished vat. The gaining of the staves, 1 inch deep, is done by hand, leaving a chime of 6 inches below the bottom. The bottom pieces are grooved and joined by a tongue ⅝ in. by 1½ in. All joints of staves and bottom must be fitted with precision and are finally put together with a thick coat of white lead.* These precautions are imperative in order to obtain air-tight vats, so that the Körting injectors may be used with effect when assisting drainage. The hoops are made of 1-inch round iron, with threaded ends passing through cast-iron lugs. The hoops

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* Experienced tank builders prefer dowel-pins to tongue and groove. Others think white lead should not be used, but tar, if anything. Russell thinks a proper vacuum cannot be obtained without jointing with white lead.

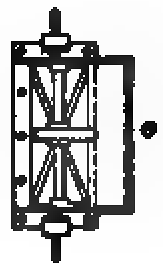


FIG. 6

are tightened by hexagonal nuts, which engage the threaded ends."

Fig. 6 (*a*) shows a plan and Fig. 6 (*b*) a section of a lixiviating vat. In the figures, *a* are staves, gained at *b*, to receive the bottom pieces; *c* is the discharge gate for tailings; and *d* is the pipe for draining off the solution. The tailings chute *e* for receiving the exhausted tailings is also shown, as well as the three-compartment launder *f* and the hose *g*.

59. Filter Bottom.—In Fig. 7 (*a*) wooden slats *a*, 1½ inches high and 1 inch wide, are laid 1 inch apart and are fastened to the bottom of the tank *b* by screws *c*, for the purpose of forming a filter. The slats are notched at *d* ½ inch deep and 2 inches wide, so that the solution can circulate freely below the filter. A space *e*, 1⅜ inches wide, is left between the ends of the slats and staves. A circular piece *f*, 1½ inches high and 1 inch wide, is fastened to the ends of the slats, leaving a ⅜-inch space *g* between the strip and the staves.

60. Filter Covering.—In Fig. 7 (*b*) the framework is covered with one thickness of matting *a*, cut just to come to the edges of the filter frame. This is covered by an 8-ounce canvas duck *b*, cut 6 inches larger than the diameter of the tank and kept in position by forcing packing *c*, made of ½-inch hemp

Fig. 7

rope, into the space between the tank and the filter frame.

61. Tanks.—There is one outlet in each tank. It consists of a cast-iron flange, into which is screwed a pipe having a tee and elbow, to which the rubber hose is connected for drainage purposes.

The tops of the precipitating tanks *B*, Fig. 4 (*a*), are about 4 feet below the bottom of the leaching tanks, to allow drainage by gravitation.

The sump tank *D* has a box and strainer around the outlet. This box is 6 inches high and has a perforated top, which prevents the solution being drawn down below 6 inches, thus keeping back sediment and chips from the storage tanks.

The storage tank *E* has no box around the outlet, as the sulphide precipitate is removed from this tank to the pressure tank *K*, from which it is passed into the filter press *L*, where it accumulates in sufficient quantity.

The tank *I* for the preparation of sodium sulphide is made of $\frac{9}{16}$-inch boiler iron. The two tanks *J*, *J* are for the storage of sodium-sulphide solution after it is manufactured in tank *I*. The solution passes from the tank *I* through to the storage tanks *J*, *J*.

62. The Pipes.—The sizes of pipes are given in the drawings. Iron pipe is affected by the solution between the outlet of the leaching tanks and the precipitating tanks; therefore, six-ply steam hose is used in this place. Wooden plugs are used for stopping the end of the hose. There are two pieces of hose leading from the center of the tank, one *u*, leading to the triple launder, the other *t* leading to the siphon pump *w*, and then through hose *v* to the triple launder *j* or *k* or *l*. There are pieces of $2\frac{1}{2}$-inch steam hose *a'* and *b'* leading from the launders *j*, *k*, and *l* to the precipitating tanks *C* and *B*.

The launder *l* and the pipe *z* are for the wash water that contains no metal salts. The launder *n* at the back of the precipitating tanks conveys the sulphides to the storage

tanks *E*. The precipitates are run into the launder by a short hose fastened to a flange on the bottom of the precipitating tank, so that all the sulphides can run out.

The launder *n* is divided between the third and fourth precipitating tanks, so that one half of the length is used to convey solutions to the pump sump and the other half to conduct the precipitated wash water out of the mill.

The launder *c* is for conducting the tailings out of the mill. The hose connection for sluicing out is shown at *y*.

The water pipe *r* is for leaching.

63. Siphon Pump.—The pump must be operated by dry steam. There is one siphon pump for each leaching tank and there is one for returning the clear solution coming from the filter press to the sump of the solution pump. If lead is precipitated, one siphon pump will be required for each of the three precipitating tanks.

CHEMICALS USED IN THE RUSSELL PROCESS

64. Stock Solutions.—Sodium hyposulphite, $Na_2S_2O_3$, is dissolved in water to form a stock solution. The strength of the solution will depend on the character of the ore and the ideas of the operator. If it be desired to make a 1-per-cent. solution, it is accomplished by dissolving 62½ pounds of sodium hyposulphite in 100 cubic feet of water, the weight of water being taken at 62½ pounds.

65. Making the Extra Solution.—Copper sulphate, $CuSO_4$, is used in the proportions of about 1 part, by weight, to 2½ parts, by weight, of sodium hyposulphite, in order to form the sodium-copper thiosulphate, or Russell extra solution. There are several sodium-copper thiosulphates, all of which answer the purpose in a measure, but the proportions just given are stated to give the best satisfaction.

66. The Le Blanc Process. — Sodium carbonate, Na_2CO_3, or soda ash, is employed for the purpose of precipitating lead as lead carbonate. It may be manufactured by the **Le Blanc** process as follows:

1. Sodium chloride is converted into sodium sulphate by sulphuric acid:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

2. The sodium sulphate thus obtained is heated with charcoal, which reduces it to sodium sulphide:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

3. Sodium sulphide heated with calcium carbonate will produce sodium carbonate and calcium sulphide:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

Calcium sulphide is insoluble in water, while sodium carbonate is soluble, and may therefore be dissolved out of the precipitate and evaporated.

67. Strength of Solutions.—At new mills it is probably best to start with a 2-per-cent. hyposulphite-of-sodium solution and increase or lessen its strength as may be found most desirable for lixiviation. The solution will be weakened by wash water and condensed steam from the injectors, also by atmospheric decomposition. The extra solution that contains copper will decompose hyposulphite.

On the other hand, the solution will gain in strength by precipitating the sulphides of silver, copper, and lead with sodium sulphide, as that contains hyposulphite. Where there are large quantities of these base metals present, the solution will regain all its strength and it might even increase in strength. After the strength of the solution that acts most advantageously is determined by experience, its strength should be maintained by the addition of sodium hyposulphite to the storage tanks. These solutions should be made fresh when needed, as they deteriorate by standing.

68. Storage Tanks.—There are three storage tanks, the use of which depend on circumstances, as follows:

First. When raw ore is treated, one of them *H*, Fig. 4 (*a*), is used for the extra solution, the other two *G*, *G* for heating and storing warm solution.

Second When roasted ore is treated, the extra solution is made up on the ore, the storage tank H being used for heating the solution, the other two tanks being used for cold-stock solution.

Third. When the plant is run to its full capacity, the storage tank H is used for the extra solution; one tank G is used for heating the stock solution, while the other one carries the cold-stock solution.

The bottoms of the storage tanks are 6 feet above the tops of the leaching tanks, to enable the liquor to flow to the latter by gravity.

The solutions are heated by about 100 feet of 1¼-inch lead pipe r', coiled on the bottom of the storage tanks and supplied with a system of valves, so that steam can be admitted to the pipes as desired.

69. Preparation of Extra Solution for Stock.—The necessary amount of sulphate of copper to make an extra solution is placed in a box with a perforated bottom above the extra-solution tank and the ordinary solution from the storage tank passed through it. Before the solution is passed through the copper sulphate, the tank is filled two-thirds full of the ordinary solution. When the copper solution passes into the tank, it meets the necessary quantity of hyposulphite and prevents the precipitation of a canary-yellow salt of cuprous hyposulphite.

The most effective extra solutions are those in which the relation between the quantity of copper sulphate and sodium hyposulphite is about 1 to 2¼. An excess of copper forms an insoluble cuprous hyposulphite salt, which is soluble in more sodium hyposulphite.

Suppose, as an illustration, it required 8 cubic feet of solution to saturate 1 ton of ore. The stock solution contains 1.5 per cent. of hyposulphite, that is, 7.5 pounds in 8 cubic feet. The ore was found by analysis to require 5 pounds of copper sulphate; consequently, in the proportion of 1 to 2¼ it would require $5 \times 2\frac{1}{4}$, or 11¼, pounds of hyposulphite. As the stock solution contains 7.5 of

hyposulphite, it will be necessary to add 3.75 pounds to bring the eight cubic feet of solution up to a normal extra solution containing 5 pounds of copper sulphate.

70. Strength of Sodium-Carbonate Solution.—The sodium-carbonate solution, Na_2CO_3, is made by dissolving in the storage tank 12 to 16 pounds of soda in each cubic foot of solution. This precipitant is used only when the extra solution has been employed to leach ores containing lead.

According to Stetefeldt, 100 parts of nearly pure sodium carbonate will precipitate 191.4 parts of lead as carbonate and 36.9 parts of lime.

71. Strength of the Sodium-Sulphide Solution.—To make the sodium-sulphide solution, from 600 to 700 pounds of caustic soda, $NaOH$, are placed in an iron tank. About 3 to 3¾ cubic feet of water are added and then steam is passed into the tank until the temperature is 200° F. The steam increases the volume of water. The total volume should be such that 1 cubic foot of solution contains 62½ pounds of caustic soda. To this lye powdered sulphur is added equal to two-thirds of the weight of caustic soda used. The sulphur is added slowly and the solution is stirred; it boils and swells in volume while the chemical action is taking place. The sulphur will dissolve completely and rapidly. If the lye is concentrated or at a lower temperature than stated above, the solution of the sulphur is not complete. The sodium-sulphite solution will solidify on cooling, and is, therefore, diluted with stock sodium-hyposulphite solution and transferred to the stock tanks. The dilution is made so that there will be as many cubic feet of the diluted solution as there have been pounds of caustic soda divided by 8.

THE MANIPULATION OF THE PROCESS

72. Washing the Ore.—To wash roasted ore, it usually takes between 20 and 80 cubic feet of water per ton of ore. The soluble salts principally removed are sodium sulphate

and sodium chloride. Besides these there may be the sulphates and chlorides of copper, zinc, manganese, iron, and calcium, also caustic lime.

The leaching is suspended when the wash water ceases to give a perceptible reaction with sodium sulphide. If the first washings should contain silver and copper in quantities worth saving, the wash water is collected in a separate tank. The silver can be precipitated by copper and the copper then precipitated with iron.

Silver chloride, cuprous chloride, lead sulphate, and antimonial salts in the solution of wash water are precipitated by diluting the solution with water. If the solution contains caustic lime, there will be no copper present, but it may contain considerable silver. In this case the lime should be neutralized with sulphuric acid and the silver precipitated by adding scrap iron.

It has been recommended in some cases to admit the wash water from the bottom until the ore is covered. A precipitate of silver chloride caused by the dilution will float on top of the vat and may be collected from the surface of the ore by scraping it off after the water is drawn off.

73. When the Roasted Ore Does Not Contain Caustic Lime, CaO.—After the ore has been washed, a quantity of the ordinary solution of hyposulphite, sufficient to replace the water, is added. The liquid running from the lixiviation vat is tested, for the appearance of the ordinary solution, with a few drops of sodium sulphide, which gives a perceptible precipitate.

As soon as the hyposulphite solution starts to come through, it is turned into the precipitating tank. Leaching is continued until the first half of the solution has passed through the ore. The quantity of extra solution, which is from 5 to 10 per cent. less than is required for saturating the ore, is next added. This prevents running any of the extra solution into the precipitating tank. The extra solution is kept circulating by means of an injector until it has done its work. It is then replaced by the ordinary solution, and

leaching with this solution is continued until the ore is exhausted.

74. When the Roasted Ore Contains Caustic Lime. In this case the ore is leached with the extra solution first. The extra solution is not circulated, but passes directly to the precipitating vat. The volume of extra solution varies between 18 and 40 cubic feet per ton of ore. This is followed with the ordinary solution, whose volume is between 20 and 90 cubic feet per ton of ore. After the ordinary solution has been replaced by the wash water, the latter is allowed to run to waste.

75. Vacuum Pump.—The Körting injector attached on the discharge pipe of the lixiviation vats produces a vacuum below the filter, which increases the rate of percolation. The injector can also be used for withdrawing the extra solution from the bottom of the lixiviation vat and returning it to the same vat, so that it produces continuous circulation.

76. Charging the Lixiviation Vat With Ore.—After the vat is charged, the surface of the ore is leveled. The ore shrinks when the solution is added. For this reason, the vats should be so filled that the ore after settling is about 12 inches from the top of the vat.

77. Treatment of Raw Ores.—Some raw ores require no "first wash water," and the extra solution is usually then applied first and followed by the ordinary solution. The extra solution is always circulated by an injector. There should be a sufficient volume of the extra solution to always cover the ore after circulation has been started. The extra solution is circulated from 4 to 6 hours. The volume required varies between 20 and 90 cubic feet per ton of ore. This is followed by leaching with the ordinary solution and washing, as described before.

78. The lixiviating solution before precipitation may contain besides gold and silver, copper, lead, antimony, arsenic, and calcium. Copper is derived from the copper in

the extra solution and copper minerals in the roasted ores. The other metals present come from the roasted ore.

79. The Precipitation of Lead.—The sodium-carbonate solution is added to the precipitating tank and the solution stirred to precipitate lead carbonate. Precipitation occurs quickly and the lead carbonate settles to the bottom of the tank. Care should be taken not to add an excess of soda, for while the presence of this reagent is not injurious to the extraction of silver, it would destroy sulphuric acid, provided caustic lime had to be neutralized. The lead carbonate is very pure. In practice, less than 1 pound of soda is consumed in precipitating 1 pound of lead.

80. The Precipitation of Silver.—The solution containing the silver is drawn from the tank in which the lead was precipitated. The solution is stirred with a paddle, while the sodium sulphide is added to throw down the silver sulphide. This reagent should not be added in excess, and in case this is done, more lixiviation solution is to be added from one of the vats. It is better to leave a slight quantity of silver in the solution than to precipitate the last trace of it.

If the solution contains lime, it is sometimes precipitated as an insoluble monosulphide, and may contaminate the precious metal sulphides. After the precipitate has settled, the clear solution is decanted into the pump sump and the precipitates are drawn into the filter-press sump.

REFINING SULPHIDES

81. Collecting the Sulphides.—The composition of the sulphides precipitated vary considerably, owing to the nature of the ore. The ordinary sulphides precipitated from roasted ore contain between 18 and 35 per cent. of silver. These are collected by filter presses on filter cloths and placed in large iron pans with the cloths. The pans with their contents are placed in drying ovens, to thoroughly dry the precipitates for subsequent pulverization in a revolving barrel.

82. Roasting the Sulphides.—The precipitate is next roasted in a reverberatory furnace at a low temperature, to drive off the sulphur as sulphur dioxide and possibly as some sulphur trioxide.

When the roasting is complete, the mass consists of a matte containing metallic silver, copper in a fused condition, copper sulphide, and some copper oxide. This matte is broken up, placed in graphite crucibles, and melted into low-grade bullion and high-grade copper matte.

The refining of such sulphides is usually carried on in smelters equipped for the purpose, but in some locations electrolytic and fire refining can be carried on to great advantage. There is a loss from volatilization in producing refined bullion. More perfect roasting would lessen the proportion of matte, but would produce a lower grade bullion and further increase the losses from volatilization.

83. Scorification of Sulphides.—A second method of refining sulphides is by scorification on a bath of molten lead and subsequently cupeling the lead. This process is more general, especially where there is a large output of sulphides, and is more advantageous to refine than ship to smelters. One method of scorification is to use a circular hearth 6.5 feet in diameter. Lead to the amount of 5 tons is melted in this hearth, and after it becomes well covered with litharge, 150 to 200 pounds of the sulphides is added with a ladle and covered with 3 times its weight of litharge, PbO.

As soon as the mass becomes melted, a blast is turned on and the scum slagged and skimmed off, after which the blast is turned off and another lot of the sulphides added to the bath. Sometimes the amount of copper is so great that soft lead has to be fed with the sulphides in order to keep them in condition.

REMOVING LEAD FROM SILVER

84. Litharge or lead oxide, PbO, is formed in large quantities in the process of separating lead from silver. In order to remove the last portion of lead from silver, the

melted alloy has air blown upon it. The lead under such circumstances is converted into oxide, while the silver remains unchanged. The litharge found in the market is produced this way and usually contains some silver. This accounts for the litharge of commerce nearly always containing silver. (See *Assaying*.)

MATTE REFINING WITH SULPHURIC ACID

85. The **matting sulphuric-acid process** of refining sulphides is a combination of wet and dry processes, which is accomplished by five operations.

(*a*) The first operation consists of fusing the sulphides in an iron pot at a low-red heat and pouring the fluid mass out into shallow cast-iron molds about ¼ inch deep, so that it will get brittle and pulverize. This matte may be crushed in any suitable pulverizer or ball mill to 40-mesh screen.

(*b*) The pulverized sulphides are next roasted as a second step in the process. The roast takes about 8 hours and is continued until a sample dropped into a beaker of water looks black. The small black lumps should be black throughout and not show a reddish center. This roasted matte is cooled and pulverized to pass through a 40-mesh screen.

(*c*) The third step in this method of refining is to dissolve the roasted matte. For this purpose, two lead-lined tanks 3 feet 6 inches in diameter by 5 feet 8 inches high, with conical bottoms closed by rubber plugs, are required. Each charge contains 300 pounds of pulverized roasted matte, together with 16 cubic feet of mother liquor from the bluestone vats, and with sufficient sulphuric acid added to make 2 pounds of sulphuric acid, H_2SO_4, present for each pound of copper in the matte. The solution is first put in the vats and steam turned on, through a steam pipe of lead terminating in the vats. The matte is next added gradually and boiled for 2 hours. Copper plates are suspended in the tanks, as an extra precaution, to make sure that all the silver is precipitated, although there is probably enough

ruby copper, Cu_2O, present to decompose all the silver sulphate. The solutions are drawn off and run through asbestos filters by a pressure pump.

(*d*) The next operation is to collect the liquor passing through the filters in lead-lined vats 6 feet long, 3 feet wide, and 2 feet deep. The sheet lead for such tanks is termed 6-pound lead, that is, it weighs 6 pounds per square foot. In these vats strips of lead are suspended, to hasten the crystallization of copper sulphate from the liquor. The mother liquor, or that remaining after the copper sulphate has crystallized out, accumulates in time iron and other impurities, and the copper is then precipitated by scrap iron as cement copper.

(*e*) The accumulated silver precipitated by operation (*c*) is washed with hot water, until the hot water issuing from the tank in which the silver was placed shows no blue coloration on the addition of ammonia. The washed silver is dried and then pressed in a hydraulic press into flat cakes 6 inches in diameter, weighing 7 to 9 pounds, which melted down in crucibles in the ordinary melting furnace yield silver bars about 950 fine.

THE CHLORINATION PROCESS

HISTORY OF THE PROCESS

1. Introduction.—Professor C. F. Plattner advocated the use of chlorine gas as early as 1848 for the treatment of gold-bearing ores. The **Plattner** process was introduced in California in 1857, and met with great success in treating concentrates.

The methods followed were not such as are usual today in all cases, but the principles were the same. The ore or concentrates were placed in vats upon a false bottom, which answered as part of a filter. The vats when charged with ore were covered over and made practically air-tight. Chlorine gas was generated outside and pumped into the vat through a hole in the bottom. The gas gradually permeated the ore from below upwards, and after several days water was admitted and the trichloride of gold, $AuCl_3$, formed leached out. The trichloride-of-gold solution was conveyed to precipitating tanks and there thrown down as a brown powder by ferrous sulphate, $FeSO_4$. Hydrogen sulphide, H_2S, and charcoal were also used later on as precipitants.

2. In the **Delacy** process, an air-tight revolving barrel was substituted for the Plattner vat. This improvement, which was patented in 1864, made an advance in the right direction, in that it considerably shortened the time required for chlorinating a charge of ore.

3. The **Mears** process, which was patented in 1877, substituted a lead-lined iron barrel for that used in the Delacy

process. The ends of the barrel were provided with hollow trunnions and goosenecks, through which the chlorine was forced into the barrel by a pressure pump. It was believed that chlorine gas under pressure was more effective and also increased the rate of changing the gold into chloride, and for that reason from 30 to 40 pounds pressure was carried on the barrel. The percentage and rate of extraction have been duplicated without such great pressure. The leaking gooseneck and pressure pump have, therefore, been universally discarded.

4. The **Theis** process, which next followed, dispensed with the hollow trunnions, gooseneck, pressure pump, and outside generation of chlorine gas. This process, while more recently improved in certain details, is the foundation for modern barrel chlorination of gold ores. The gas for this process is generated in the barrel charged with ore. The chemicals used for generating the chlorine are bleaching powder, $2CaOCl_2$, and sulphuric acid, H_2SO_4, and they are placed inside the barrel with the ore.

5. Comparison of Methods.—The **vat** process, while requiring no power, had this advantage offset by the time saved and the increased capacity of the barrel method. The decrease in the consumption of chemicals and the labor of converting them into gas was also an item in favor of barrel chlorination. Recent practice has practically done away with the outside filters used in early processes, and in some instances the filters form a part of the inside arrangement of the chlorinating barrel.

CHEMISTRY OF THE PROCESS

6. The Basis of the Process.—The chlorination process is based on the fact that gold is acted on slowly by chlorine to form trichloride of gold, which is soluble in water. The reaction represented by the equation is

$$Au + 3Cl = AuCl_3 + Cl$$

When a little water is added to the above, the dichloride is converted into trichloride, thus:

$$AuCl_2 + ClH_2O = AuCl_3 + H_2O$$

7. Generation of Chlorine.—Plattner used manganese dioxide, MnO_2, sodium chloride, $NaCl$, and sulphuric acid, H_2SO_4, for the purpose of generating chlorine gas. The reactions that occurred were practically as follows.

$$2NaCl + MnO_2 + 2H_2SO_4 = 2Cl + Na_2SO_4 \\ + MnSO_4 + 2H_2O$$

8. The chlorine gas for the barrel process is generated in the barrel by using bleaching powder [which, according to Remsen, has a formula of $2CaOCl_2$, and according to some other writers, $Ca(ClO)_2 + CaCl_2$] with sulphuric acid. The equation given shows the probable reaction that takes place.

$$2CaOCl_2 + 2H_2SO_4 = 4Cl + 2CaSO_4 + 2H_2O$$

9. Precipitation of Gold.—Plattner used ferrous sulphate, $FeSO_4$, for precipitating gold from the trichloride solution. Gold in such cases is precipitated as a brown powder according to the formula given:

$$2AuCl_3 + 6FeSO_4 = 2Au + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

10. In the modern chlorination plant, sulphur is burned to form sulphur dioxide, SO_2, for the purpose of driving off the chlorine that is in excess in the trichloride-of-gold solution. Thus,

$$2Cl + SO_2 + 2H_2O = 2HCl + H_2SO_4$$

In case there was an excess of sulphur dioxide, the following reaction would probably occur, thus:

$$2Cl + SO_2 + H_2O = 2HCl + S + 3O$$

After the surplus chlorine has been combined, gold may be precipitated from the solution by sulphureted hydrogen, H_2S. This reagent throws down the gold as a yellowish-brown sulphide, according to the equation given:

$$2AuCl_3 + 3H_2S = 2Au + 3S + 6HCl$$

11. Necessity for Roasting.—Part of the chemistry of chlorination includes the roasting and chloridizing of ores before they are treated with chlorine gas. The chlorination process can be used to extract gold from free-milling ores without roasting, but refractory ores and concentrates must be roasted to convert the metals into oxides, which are but little acted on by chlorine. During the dead and chloridizing roasting operations necessary to get rid of such base-metal salts as would be objectionable to the process, the silver in the ore is lost.

While roasting, arsenic, antimony, and sulphur must be removed as completely as possible. The soluble salts, such as ferrous sulphate or chloride, $FeCl_2$, must be so changed in character that they will not precipitate gold from its solution. When ores contain lime, magnesia, or lead, salt is added towards the end of the roasting to change these metals into chlorides and so prevent chlorine acting on them during the chlorination.

12. Oxidizing Roast.—The ore for this purpose is exposed to heat with an excess of air. The sulphur of the sulphurets is set free and combines with the oxygen of the air, forming sulphur dioxide. The metals, by losing part of their sulphur, are converted into oxides and sulphates. *Nearly all of the silver is converted into a sulphate or reduced to the metallic state.*

Arsenic and antimony are partly oxidized to pass off as arsenic trioxide, As_2O_3, and antimony trioxide, Sb_2O_3, while a part remains to combine with the metal oxides to form salts of antimony and arsenic.

13. Dead Roast.—The sulphate of iron usually predominates, and as this will precipitate gold from a solution of the chloride of gold, it becomes necessary to remove it. This is accomplished by increasing the heat of the furnace and decomposing the sulphates into oxides. It is comparatively easy to drive off sulphur to 2 per cent., but below this it is difficult and requires extra care. The expense of getting rid of the last 2 per cent. of sulphur is greater than in getting

rid of the first 25 per cent. The order in which some of the sulphates are decomposed is iron, copper, and silver. Lead sulphate is not decomposed. After the sulphur, arsenic, and tellurium have been removed, the gold remains in a free metallic state and can be detected by panning.

14. Chloridizing Roasting.—At first this is the same as the oxidizing roasting, but salt, $NaCl$, is mixed with the ore some time during the operation. The quantity of salt required depends on the kind of ore being treated and varies from 1 to 2 per cent. of the ore. Chlorine liberated from salt under the action of heat combines with the metals present to form metal chlorides or with substances such as lime and magnesia. During a chloridizing roasting, gold is not vaporized, but it may be carried off mechanically in fine dust by other vapors and the draft. On the other hand, in roasting ores containing silver with salt, great care is necessary to prevent the loss of silver.

15. Working Tests.—The chemistry of the chlorination process is simple to understand, and by close attention to details a fair test of ore, which may answer as a working test, can be made in the laboratory. The quantity of ore taken for working tests should be several pounds, while the chemical tests for availability of ore requires but several assay tons. After a working test has given results that are satisfactory both in leaching and roasting, a mill can be erected without much danger of going amiss in the conclusions.

LABORATORY TESTS

16. Ores Suitable for the Process.—In order to determine whether an ore is suitable for the chlorination process, it should be subjected to the following laboratory tests:

1. The ore should be assayed to ascertain its gold value, and it probably should be assayed to determine the percentages of base metals it contains.

2. A quantity of ore is to be weighed, roasted dead, and reweighed.

3. The roasted ore should be saturated with chlorine gas, then with water, and the solution obtained drained off after standing several hours. This operation will extract the gold.

4. Wash the tailings left by the third operation and then dry and assay them. This will give the gold value remaining after extraction by chlorine.

5. Precipitate the gold from the solution and refine the precipitate.

17. Assaying the Ore.—The ore is assayed by some one of the methods touched upon in *Assaying*. The difference between the ore assay and the tailings assay should give the extraction, and the refined precipitates should give a pretty close check. Usually, it is possible to obtain high extraction by the chlorination process, so high, in fact, that some custom chlorination mills guarantee 95 per cent. and others 92½ per cent. extraction, charging $7 per ton for treatment.

18. The Roasting Test.—For the second test, from 15 to 25 assay tons of pulverized ore are placed in an iron pan. This pan is inserted into a muffle furnace and the ore given a dead roast. To ascertain whether the roast is perfect, some of the roasted ore is put into a beaker containing water and stirred. After allowing the ore to settle, a part of the clear solution is taken and tested with a few drops of potassium ferrocyanide, $K_4Fe(CN)_6$. If the ferrocyanide solution produces a green or blue coloring, the roasting is not perfect.

To test for copper, take part of the clear solution in which the ore was stirred and add a few drops of ammonia. If a blue color is obtained, copper is present in the solution. Weigh the roasted ore and ascertain the loss it has sustained by roasting

19. Chlorine Test.—Treating with chlorine is the next test, and for this purpose weigh a quantity of roasted ore

crushed to pass a 30-mesh screen that would correspond to 10 A. T. Put this ore in a glass bottle and add 10 grams of dry bleaching powder; then add water to make a pulp having the consistency of thick mud. Mix 90 c. c. of water and 10 c. c. of strong sulphuric acid in a small beaker and then pour this dilute acid into the bottle containing the ore. Cork the bottle with a rubber stopper having a hole in it that may be closed with a piece of glass rod. Tie the stopper down, wrap the bottle in a towel, and agitate occasionally during a space of from 4 to 6 hours. Remove the stopper, and if there is no smell of chlorine, add 10 grams of bleaching powder and 10 grams of sulphuric acid. Close the bottle and agitate at intervals during the next 4 to 6 hours.

Remove the stopper at the end of the second period and test for chlorine by the smell. If chlorine is present, it may be taken for granted that the maximum extraction has been reached. If free chlorine should not be present, it will be necessary to add more chloride of lime and sulphuric acid and repeat the agitation.

If chlorine is present, add water; pour the contents of the bottle on a filter paper and wash with water into a bottle or beaker until all the soluble salts are removed. Collect the gold solution and wash water for the recovery of the gold.

20. After the foregoing operations have been completed, dry the tailings in an air bath, weigh, and note the loss in weight. Assay the tailings for gold in the usual way.

21. The last operation is to precipitate the gold from the solution, and to do so, heat the solution to remove all free chlorine; then add a clear solution of ferrous sulphate until all the gold is precipitated. This can be determined by failure to precipitate more gold on the addition of a little more ferrous sulphate after the first precipitate has settled. Filter the precipitated gold and place the filter paper containing the gold in a scorifier with test lead and borax mixed in the proportions suggested in *Assaying*. Fuse the charge and pour into a mold, remove the slag, cupel the button, and

weigh the gold. This operation will give the gold in the solution.

22. Time Test.—To determine the time it will take to treat an ore, another laboratory test can be made. For this purpose, take six wide-mouthed bottles, each holding about 8 ounces; fit them with rubber stoppers having holes that may be closed with glass rods.

Place in each bottle 10 grams of ore and 90 c. c. of water; to this mixture add 5 grams of bleaching powder and 5 c. c. of strong sulphuric acid. The bottles should be tightly stoppered and shaken frequently. At the end of 2 hours the contents of the first bottle is emptied on to a filter and leached rapidly with water into a beaker. At the end of 3 hours and every subsequent hour, one of the remaining bottles is emptied and the liquor filtered into a beaker. The tailings from each bottle are washed and dried and then assayed. The results obtained will show the time best suited for economical extraction.

23. Testing Solutions for Gold.—To test a solution for gold, take a little of the trichloride solution in a test tube. To this add a solution of sodium sulphide, Na_2S, and the presence of gold will be indicated by a dark-brown or black precipitate. If the precipitate is small, it may be more easily detected by taking two test tubes. One is filled with water and the other with the gold solution. Add the solution of sodium sulphide to both tubes; shake and then look down through the length of the test tube from above, with a white surface as a background; any slight change of color may be detected by comparison.

CONDITIONS FOR SUCCESSFUL CHLORINATION

24. With many ores the chlorination process is very successful, but the following requirements have to be carefully observed:

1. The gold must be in a metallic state. Quartz containing very fine gold and free from other minerals and

sulphurets can be chlorinated without roasting. Ore containing sulphurets requires dead roasting. All metals, except gold, must be transformed into oxides.

2. The chlorine gas used must not contain hydrochloric acid, as that will dissolve the oxides; and when sulphides are present, as the result of defective roasting, they generate sulphureted hydrogen, which precipitates the gold.

3. There must be no substances associated with the ore that will unite with free chlorine, as they would occasion a loss of gas and a probable failure in gold extraction.

4. No reaction must take place in the mass treated with chlorine that will prematurely precipitate the gold before the final solution is drawn off.

5. It is desirable that all the gold be retained in the final solution and, if possible, nothing else.

THE PLATTNER PROCESS OF CHLORINATION

25. Vat Construction.—The **Plattner process,** although at present little practiced in the United States, will be taken up and discussed first, for even at this date the student should commence at the beginning.

In Fig. 1 is shown a vertical cross-section of a wooden chlorinating vat and cover. In the figure, *a* is a wooden trestle for supporting the vat stringers *b*. The staves of the vat are represented by *c*, the bottom by *d*, and the hoops by *e*. The cover *f* is shown suspended from a beam *g* by block and fall *h* and the hooks *i* and *j*. The vat contains a false bottom *k* of 1-inch boards, through which half-inch holes are bored at intervals of about 4 inches on the flat sides. The boards are laid loosely at right angles on 1-inch wooden strips *l*, by means of which they are separated from the bottom of the vat. The wooden strips do not extend clear across the vat bottom, but are broken at intervals, and not carried so as to touch the sides of the vat, the object being to afford free circulation of the liquor that passes below the boards and also for chlorine gas. On the false bottom is

placed a layer of pebbles about 4 or 5 inches deep, the pebbles being just large enough not to fall through the holes.

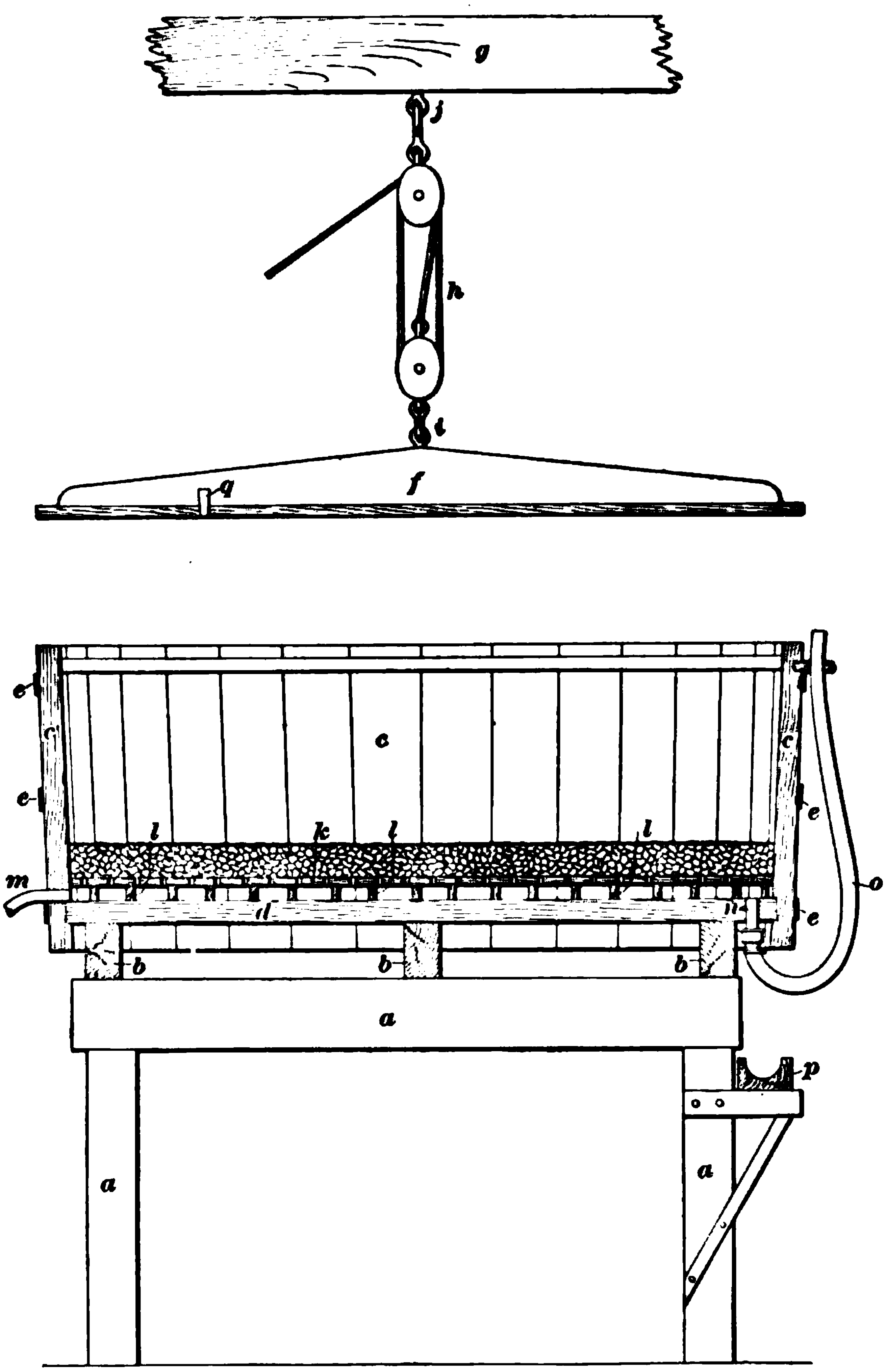


FIG. 1

Over the pebbles a layer of burlap or asbestos cloth is spread and in some cases sand. There are two holes in the

vat below the false bottom. The hole *m* has a lead pipe tightly fitted into it, through which chlorine is introduced into the tank. The hole *n* has an attachment for the rubber hose *o*; through it the solutions are drained into a launder *p*, by which they are conducted into the precipitating tank. The cover *d* must fit tightly, and it is then caulked with asbestos or fireclay, or both. The block and fall *h* mentioned could now be safely exchanged for a modern differential chain hoist.

26. Plattner Chlorine Generator.—To produce chlorine gas for the Plattner process, an outside generator was required. Such a gas-producing apparatus is shown in section in Fig. 2. In the figure, *a* is a lead vat having double

FIG. 2

sides *b* on its upper half, so arranged as to hold water and form with cover *c* a gas-tight joint. The water in the channel *b* should be at least 6 inches deep. The projection at *d* is plugged when chlorine is being generated and opened to remove exhausted material. The stirrer *e* is turned by a handle *g* from time to time, when acid is poured into the chamber through the pipe *i*. The opening *h* is closed by a wooden plug and is opened only when introducing solid chemicals. The collar *f* forms with the curtain *c* a rest for

the stirrer, thus permitting it to bear lightly on the bottom of the vat. The pipe *k* conducts the gas from the tank to pipe *l*, thence into wash bottle *o*, and from there through pipe *m* to pipe *n*, and so on to the leaching vat.

27. The wash bottle *o*, mentioned in the preceding article, is fitted into the keg *p*, so as to be air-tight at their junction. The pipe *l*, which is seen passing below the surface of the water in the barrel, is made of rubber and is placed in the position shown in Fig. 2 so that the gas may be washed before it is passed into the leaching vat. The gas as it is delivered by tube *l* rises up through the water into bell jar *o* and so out through pipe *m*.

28. Precipitating Tanks.—The next piece of apparatus to discuss is the precipitating tank, an old style of which is shown in Fig. 3. It is a wooden tub, with the staves *a*

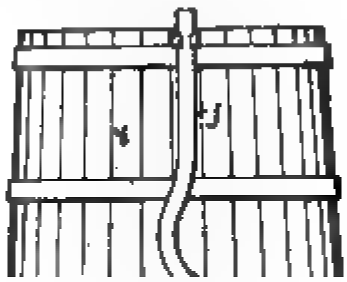


FIG. 3

coated with tar. The bottom *b* has a greater diameter than the top, to prevent the precipitate settling on the side.

The waste solution, after the precipitate has settled, is removed by a rubber hose *c*, with a wooden float *d*, attached at one end, and a pipe *e*, fastened to the other. When not in use, the hose is fastened to the inside of the vat, as shown by the dotted lines. The object of the float is to siphon off the thin solution from the top down and not allow the nozzle of the hose to sink so low on the bottom as to drain off any of the precipitates *f*. The opening *g* has a spigot or plug cock inserted in order to draw off the precipitates into a sink *h*.

29. The small vat *i*, shown above the precipitating vat *a*, contained a solution of iron sulphate, $FeSO_4$, for throwing down the gold held in solution in vat *a*. The solution was mixed with the trichloride solution by means of the hose *j*. When not in use, the hose was turned upwards and fastened to the side of the tank, as shown in the figure. The only remaining apparatus needed for the Plattner process, to make the description complete, would be the bullion furnace, which does not differ from bullion furnaces at the present time. Its description may be found in Art. **48.** The next step in order is to describe the process as it was practiced.

30. Charging the Leaching Vat.—Before charging the vat, a layer of dry ore was sifted over the filter bottom to absorb the moisture from the previous leaching. If this were not done, the ore would become too wet to allow the gas to permeate the mass and cause a large consumption of gas to no purpose. The ore was next dampened with water and thoroughly mixed, after which it was sifted into the vat so as to be a loose, porous mass through which the chlorine gas could make its way. The object of dampening the ore may be understood better by stating that dry chlorine gas scarcely attacks gold, but a saturated solution of chlorine water readily attacks the precious metal, provided no other substance for which it has greater affinity be present. The ore was sifted into the vat until it was within 6 inches of the top, after which the cover was put on and luted at the

joint with clay or other plastic material capable of making an air-tight joint and not acted on by chlorine.

31. Charging the Generator.—The next step in the process was to generate gas by placing sodium chloride, manganese dioxide, and water into the chlorine generator shown in Fig. 2. These chemicals having been mixed by the stirrer, the generator was warmed, then a portion of sulphuric acid added, and the whole mixed with the stirrer. It may be stated here that the leaden generator *a*, shown in Fig. 2, rested upon a water or sand bath *q*, some distance away from the fire, on grate bars *r*. These precautions being taken, there is little danger of the generator melting down. When the gas was disengaged, it could be seen to pass through the wash bottle, and whenever it decreased in volume more acid was added and the mixture stirred. The charge inserted into the generator to evolve sufficient gas for 3 or 4 tons of roasted ore was as follows: Manganese dioxide, MnO_2, 30 pounds; sodium chloride, $NaCl$, 40 pounds; water, 36 pounds; sulphuric acid, H_2SO_4, 66° Beaumé, 70 pounds.

32. Dissolving the Gold.—As soon as the gas was given off by the chemicals in the generator, it passed, as already stated, through the leaden pipe *m*, shown on the side of the vat in Fig. 1. The small hole *q* in the cover of the vat was left open to permit the displaced air to escape. The same opening was used to test for the presence of chlorine gas above the ore. When the gas had passed through the ore and collected in the air space above the ore, it would produce intense white fumes with ammonia, showing that the ore was saturated with gas, or else it was passing through the ore too quickly to be absorbed. The hole *q* was then plugged and the gas passed into the ore for 1 or 2 hours longer. The ore and gas were left in contact from 6 to 40 hours undisturbed.

33. After it had been judged that sufficient time had elapsed for the gold to be dissolved, the plug hole *q*, Fig. 1, was opened and the ammonia test for chlorine gas made.

Were no ammonia chloride fumes given off as a dense white cloud, the chances for a low extraction of gold were considered good; for, either there had not been enough chlorine admitted to more than extract the gold or some other substance was using up the gas. On the other hand, it was argued that an excess of chlorine gas in the tank indicated a good extraction, because no more gold was present for its absorption. Free chlorine gas that remained after the operation was drawn off with the ordinary gas pump through the lead pipe *m*. Water was next added in sufficient quantity to cover the ore and was then drained off into the precipitating tank. More water was then run on until the solution coming from the tank showed no trace of gold when tested. Some operators allowed the water to enter the vat at the same rate that it drained off, in order to save time.

34. Ferrous-Sulphate Precipitation.—Precipitation of the gold followed leaching, and for this purpose ferrous sulphate was placed in the precipitating vat before the leaching began. The gold solution entered the precipitating tank and was precipitated as a brown powder, which slowly settled to the bottom of the tank.

The solution was tested for complete precipitation and the gold allowed to settle to the bottom of the tank. The mother liquor was drawn off by a floating siphon and the gold allowed to remain in the bottom of the tank. Fresh ferrous sulphate was then added to the tank and a fresh solution from the leaching vat was allowed to run into the precipitating tank. This process was repeated until sufficient gold precipitate had accumulated to warrant a *clean-up*.

35. The Clean-Up.—The clean-up, or the collection of the gold precipitates, followed. The clear liquid was drawn off as closely as possible to the precipitates and the slimes scooped on to a filter of canvas or passed through a filter press. The precipitates were then washed thoroughly with water, after which they were pressed into filter bags, then transferred to an iron pan, and almost, but not completely,

dried in a furnace. While the precipitate was drying it was mixed with a little powdered borax and niter. The object for not drying the precipitate completely was to prevent it from dusting when transferred to the melting pot. If several ounces of niter were added to the precipitates, about half as much quartz was also added to prevent the destructive action of the niter on the melting pot during the melting of the gold.

36. The fluid gold was poured from the plumbago crucibles in which it was melted into molds. After cooling, the slag was removed and the bullion remelted with a little borax, so as to obtain a uniform bar. The slag was then crushed, mixed with a little borax, and melted, after which it was poured into a conical mold, so that any gold which it might contain would settle into the sharp end of the mold.

MODERN BARREL CHLORINATION PLANT

MODERN PLANT DESIGN

37. Description of Chlorination Plant.—In Fig. 4 is shown the elevation of a modern chlorination plant. In the design, the ore fed to crusher *a* is intended to fall into the elevator boot *b*, from which it is raised by the elevator buckets and discharged into spout *c*. The spout leads the ore to a revolving drying furnace *d*, from which it is carried by a spiral conveyer *e* to crushing rolls *f*. From the crushing rolls the ore slides down a spout *g* into a boot *h* and is raised by an elevator to revolving screens *i*. The screened ore falls into the ore bin *j*, beneath which there is a trough *k*, in which a spiral works that conveys the ore to the roasting furnace *l*, Fig. 5. That ore which was too coarse to pass through the revolving screens *i*, Fig. 4, is returned by gravity to the crushers, after which it is raised by buckets to screen *i*, from which it falls—if fine enough—into bin *j*, and so on to the roaster. The roasting furnace *l*, Fig. 5, works

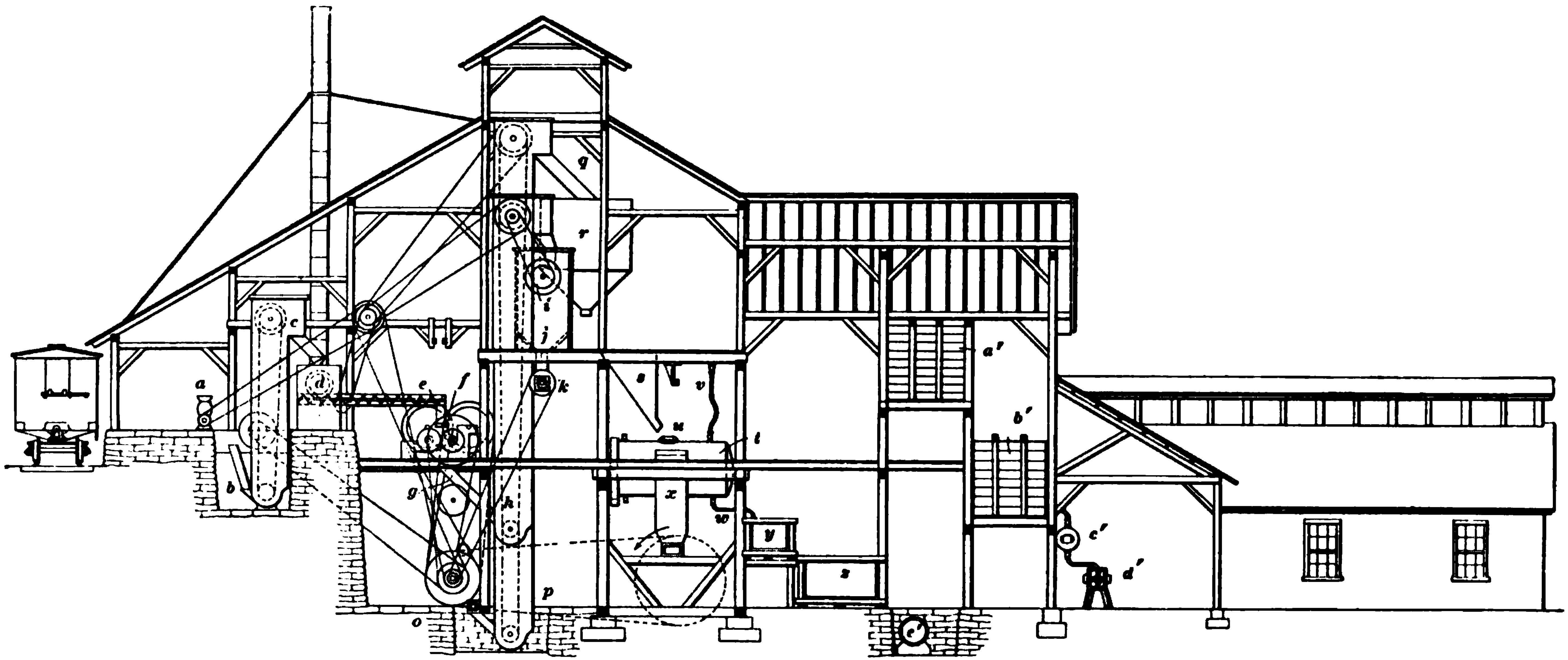
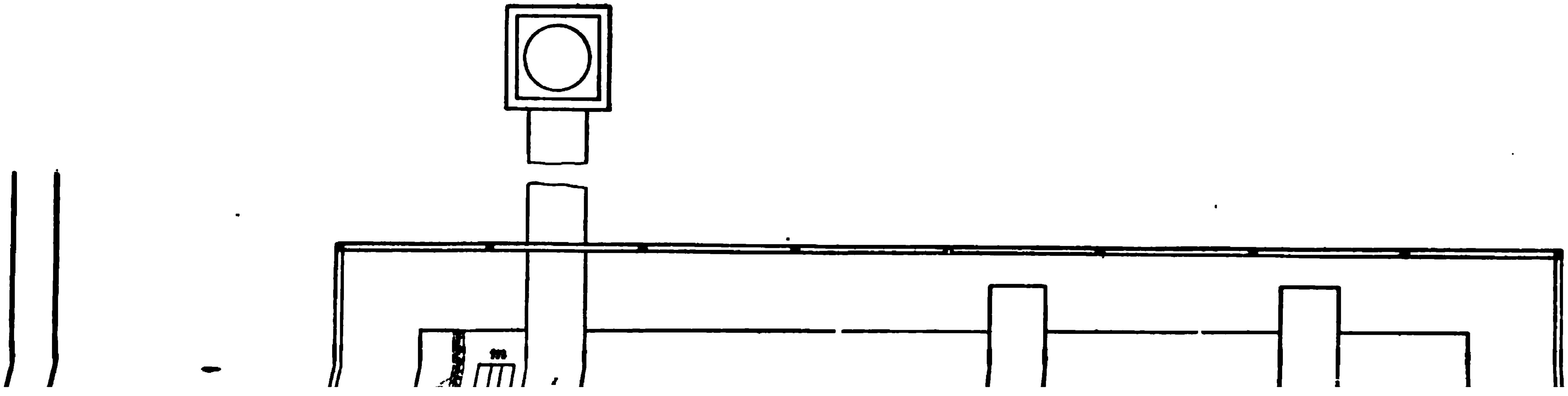


FIG. 4



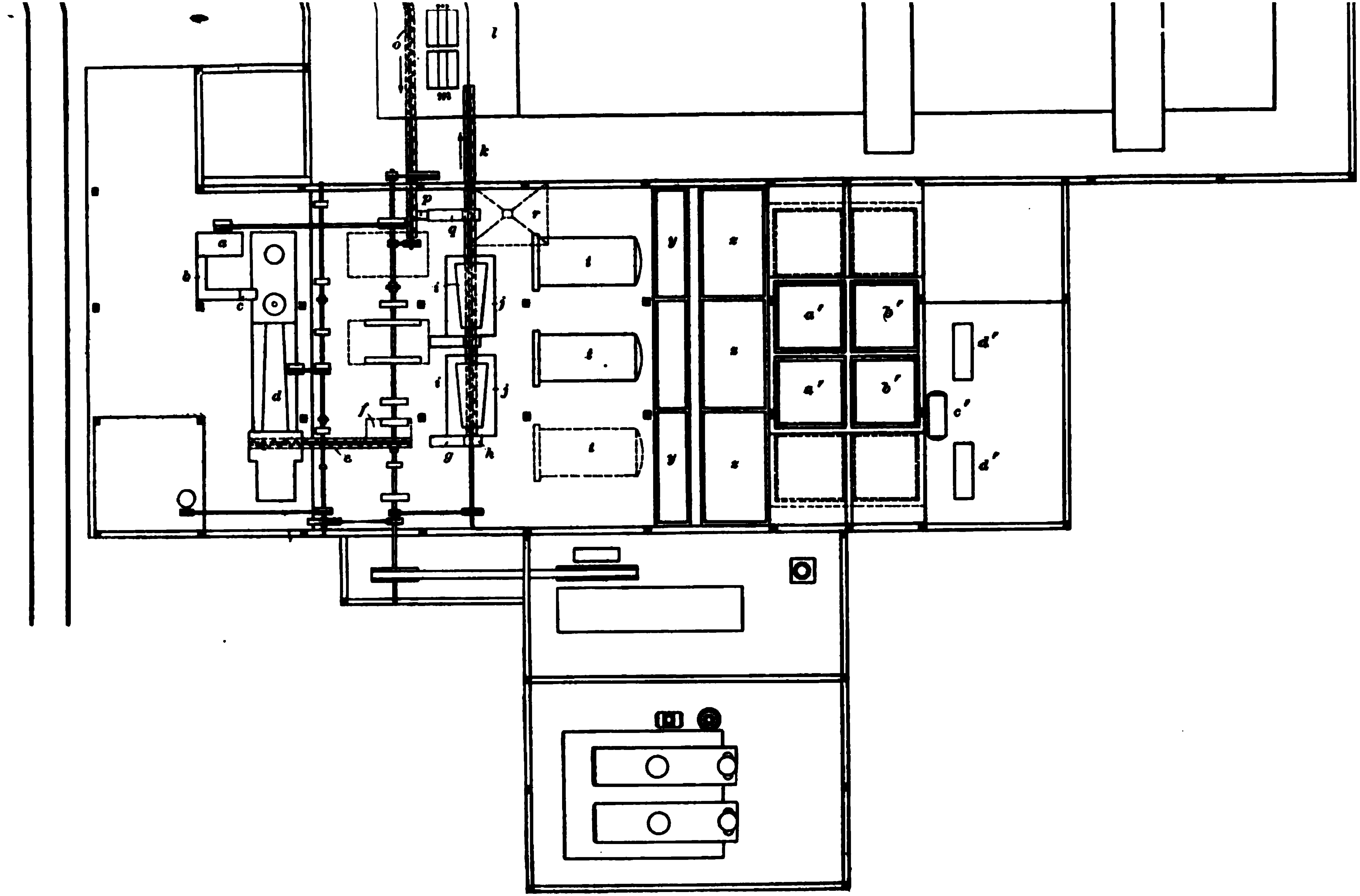


FIG. 5

automatically and discharges the roasted ore, by means of rakes or rabbles, on to a cooling floor *m*, from which place a spiral conveyer *o* takes it to the elevator boot *p*. The elevator buckets entering boot *p*, Fig. 4, raise the roasted ore to the discharge spout *q*, down which it slides into the hopper or bin *r*. From the bin *r* the ore is drawn off as desired into the barrel-loading spout *s*. The spout *s* is made large enough to hold the proper charge of ore for the chlorinating barrel *t*. The chlorinating barrels are charged with ore, chloride of lime, and sulphuric acid through the manhole *u*, whose cover is made to easily close tight with a latch.

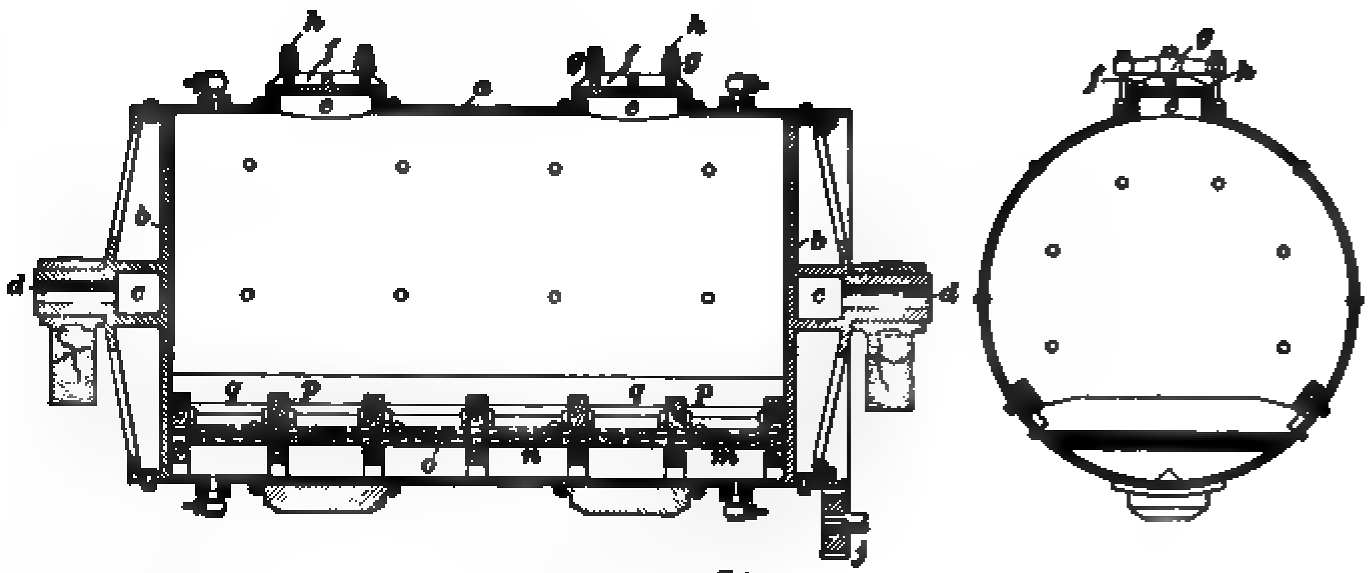
38. The barrels *t* are revolved by means of gearing, which is shown in Fig. 6 (*a*). When it is desired to filter or draw off the trichloride-of-gold solution, the pipe *v*, Fig. 4, is attached to the barrel, also the pipe *w*. Air is forced through pipe *v*, which presses on the liquor and drives it through the filter shown at *m*, Fig. 6 (*b*). The liquor which has passed the filter flows out of the barrel through pipe *w*, Fig. 4. The liquor having been drained from the barrel and the wash water which follows the liquor as well, the manhole is removed and the ore dumped into trough *x*, Fig. 4, by turning the barrel half way around from its position in the figure.

39. The trichloride-of-gold solution passes from the barrel through pipe *w* into lead-lined tanks *y*, in which it is allowed to settle and then pass into tank *z*. From tank *z* the clear liquor is pumped up to the precipitating tank *a*′. After precipitation is effected and the precipitate settled, the liquor is siphoned off from the precipitate into tank *b*′, from which it flows by gravity to and through the filter press *d*′ into the drain *e*′.

40. Barrel Chlorination Mill.—A plan of the mill just described is shown in Fig. 5. In the plan, *a* is the crusher, *b* the elevator, and *c* the spout leading from the elevator head to the drying furnace *d*. The spiral conveyer *e* is

shown leading to rolls *f*. The elevator and spout to the screens *i*, as well as the spiral conveyer *k*, are shown leading to the roaster *l*. The cooling floor *m*, the spiral conveyer *o*, and the elevator leading to ore bin *r* are also shown. The barrels *t*, tanks *y*, *z*, *a'*, *b'*, and *c'* are outlined, as well as the filter press *d'*.

41. Size of Barrels.—The capacity of chlorination barrels varies from 5 to 15 tons; that shown in Fig. 6 (*a*)



(*b*)

FIG. 6

and (*b*), it is assumed, will have the former capacity. The shells *a*, Fig. 6 (*b*), of the barrel are tank steel ½ inch thick,

9 feet long, and 5 feet in diameter, inside. The cast-iron heads *b*, bolted through flange and shells, are 2½ inches thick and heavily ribbed. The hubs *c* and trunnions *d* are also part of the head. The former are 4½ inches long and 14 inches in diameter, while the latter are 12 inches in diameter and 12 inches long where the barrels are supported and turned on them. This method of revolving is not practiced much, it being considered better in large plants to revolve the barrel on rollers and thereby better distribute the weight and friction.

Large barrels, such as shown in Fig. 6 (*b*), are provided with two oval manholes *e*, 11 in. × 16 in. The manhole covers *f* are held in place by two heavy iron yokes *g* and four 1½-inch bolts *h*. The cover is fastened during charging and discharging to a swinging lever, which holds it away from the barrel. These barrels are lined with sheet lead, that on the head being ½ inch thick, while that on the shell is ⅜ inch thick. The weight of ½-inch thick sheet lead is 24 pounds and that of ⅜-inch sheet lead 18 pounds per square foot. The steel shell is made from one sheet and the rivet heads are countersunk. Flat-headed, lead-covered bolts are used for bolting the lead lining to the steel sheets.

The barrel, as shown in Fig. 6 (*a*), is driven with a spur gear *e* encircling the shell and meshing with a pinion *j*, which is operated by a friction wheel *k*. A brake *l* is provided for stopping the barrel at the desired point.

42. Barrel Filtering.—The filter bottom *m*, Fig. 6 (*b*), assumes a horizontal position when the barrel is in position for charging or filtering, and has an area of nearly 30 square feet, being 8 feet 2 inches long and 3 feet 8 inches wide. The filter consists of a sheet of perforated lead *n*, supported on wooden segments *o*, covered above with asbestos cloth, and still above the cloth with wooden grating *p*, the whole being held in place by wooden cross-beams *q*.

The filter should be porous enough to hold the pulp at the beginning of filtration and also be of a material that will

resist the action of the chemicals. After the pulp settles on the diaphragm, it forms a perfect filter of itself.

43. There are four precipitating and four storage tanks in the mill illustrated in Fig. 5. These tanks, each 8 feet square and 8 feet high, are made of wood, lined throughout with lead weighing 6 pounds to the square foot.

In the same plan there are shown three settling tanks each 3 feet high, 4 feet wide, and 14 feet long, also three storage tanks, each 4 feet high, 8 feet wide, and 14 feet long. These tanks are lined throughout with lead to preserve them from the action of the chemicals.

44. Hydrogen-Sulphide Precipitation.—The hydrogen-sulphide generator shown in Fig. 7 is constructed of light sheet steel, with angle-iron flanges and a cover *a* of cast iron. The tank, which is lead-lined, is divided by a conical partition *b*, provided with a hole *c* in its center. A lead pipe *d* is inserted through the hole in the center of the conical partition and fastened tightly to it. The acid chamber *e* is attached at the side of the generator and delivers acid below the partition. Compressed air, admitted through the pipe *f* into the lower compartment *g*, forces the acid up the central tube *d* into the upper compartment *h*, where the iron sulphide is placed. The gas escapes through *i* to the precipitating tank.

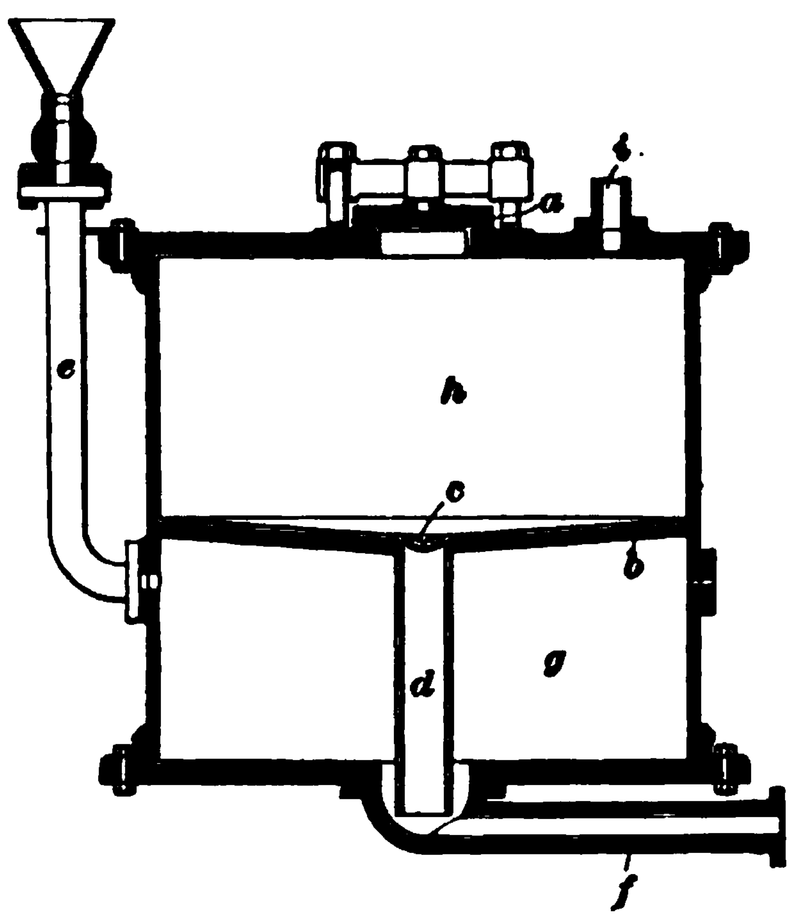


Fig. 7

45. The sulphur-dioxide generator shown in Fig. 8 is a cast-iron tank *a*, with an air-tight handhole plate *b*, that

may be easily removed. The sulphur-burning tray *c* is covered with a plate *d* and is so arranged that the compressed air admitted to the tank through *e* is compelled to pass over the burning sulphur. The gas passes into the chamber *f* and is forced through the pipe at *g* into the precipitating tank.

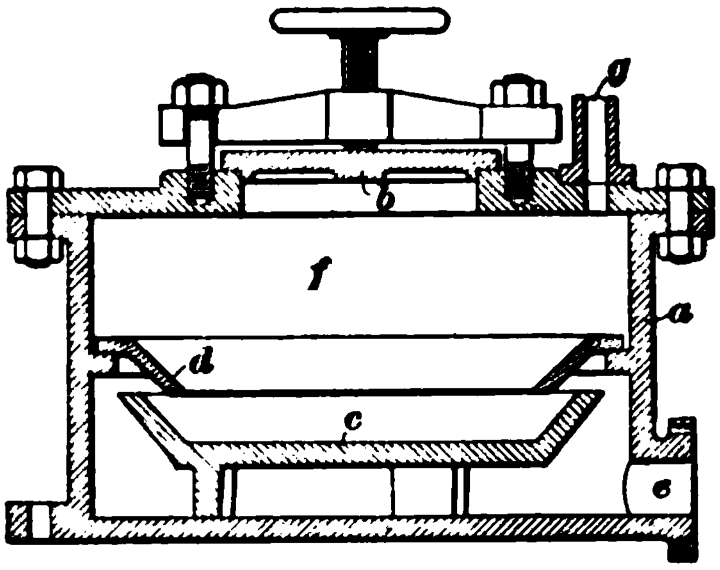


FIG. 8

46. The pressure tank shown in Fig. 9 has a $\frac{3}{8}$-inch sheet-steel shell with a $\frac{1}{2}$-inch steel head flanged. It is lined with sheet lead weighing 8 pounds to the square foot. There are two holes in the top head; one is the air inlet and the other is for the solution. There is an opening *c* in the bottom head for connection with the filter press. One pressure tank is required for each filter press. The pressure tank in a 50-ton plant should be about 700 gallons capacity. The manhole is opened to admit the gold precipitates from the precipitating tank.

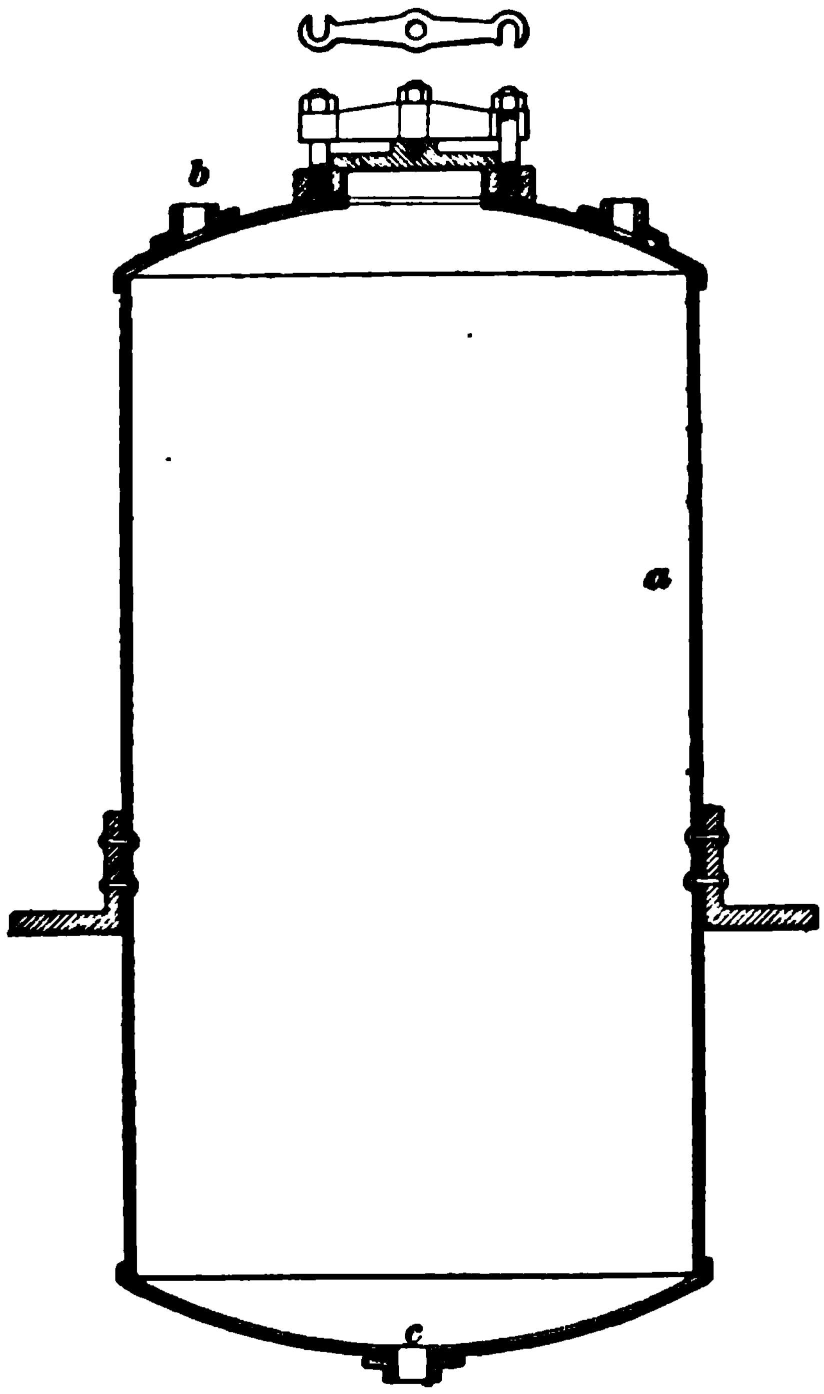


FIG. 9

47. The Filter Press. In Fig. 10 is shown a 19-inch square washing filter press, with from 24 to 36 chambers, flush plates, and distance frames. There are separate

FIG. 10

outlets *a*, which lead into a trough *b*. With these separate outlets it is possible to examine the solution from each plate and detect any break that would let the precipitate through. When a break occurs, the outlet of the imperfect chamber is stopped up until the clean-up is completed. The filtering medium is a heavy cloth mat *c*, with the nap on one side. The nap side *c* is placed next to the chamber *d*, and on this is placed a 10-ounce canton flannel with the nap side in. The filter frame should be given several coats of acid-proof paint when new and this paint should be renewed occasionally, whenever it is affected by the solution running through the press.

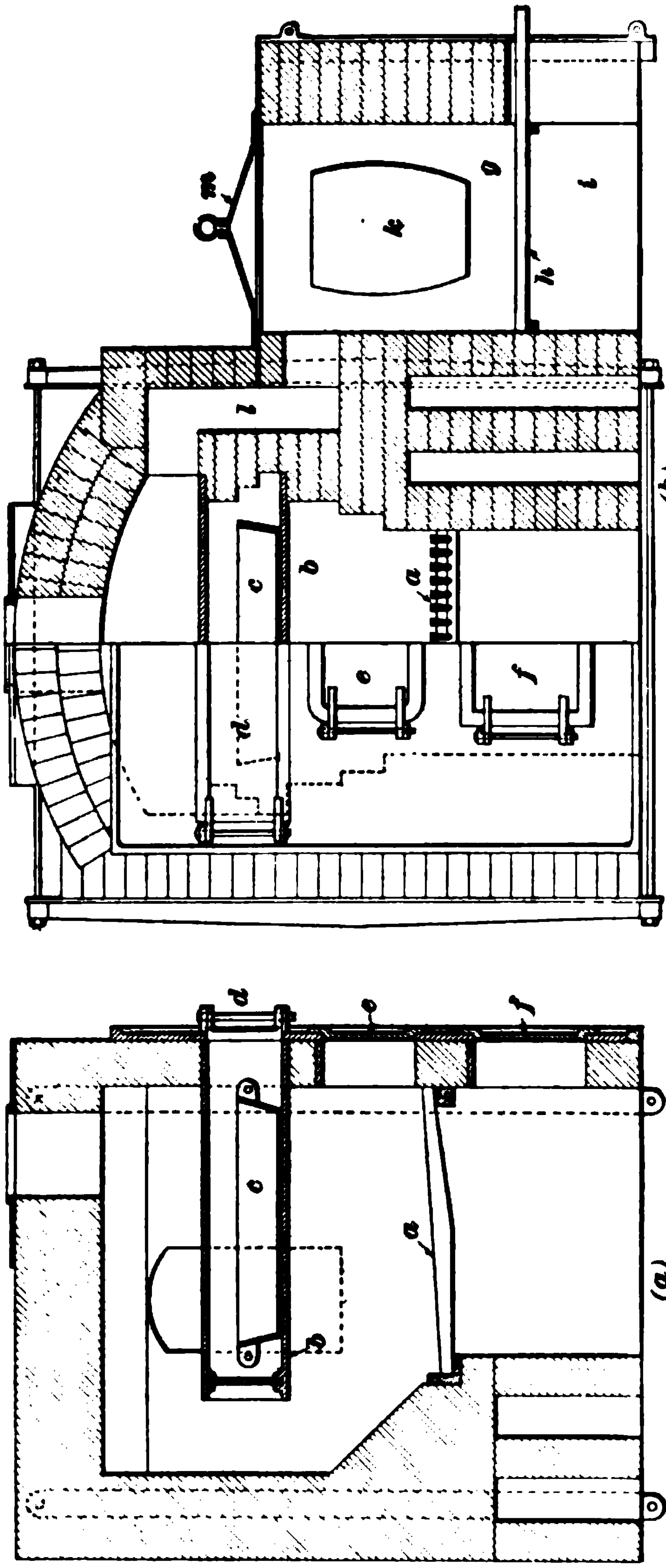


FIG. 11

Filter presses are being made of wood and are giving good satisfaction. In working the press, the solution enters at *e* and the precipitate is deposited in the space between the frames. The solution, after passing through the filter

cloth, passes through the corrugated spaces to the bottom of the frame and finally out of the frame through *a*. The wash water enters the press at *f*. After the precipitate has been washed and air passed through for a short time to dry it, the filter press is opened and the cloths removed from the frames. The cloths containing the precipitate are burned with it in the furnace.

48. Melting the Precipitates.—A combined muffle and crucible furnace, designed for roasting and melting the gold precipitates from chlorination and cyanide mills, is shown in Fig. 11 (*a*) and (*b*). The section presented by Fig. 11 (*a*) gives a general idea of the arrangement of the grate bars *a* with relation to the muffle *b*. The muffle is made large enough to receive the iron gold-slime-drying pan *c*, which is 24 inches square.

Fig. 11 (*b*) is partly a front elevation and partly a vertical cross-section of the furnace. The muffle door *d*, the firebox door *e*, and the ash-pit door *f* are partially cut away to show the position of the grate bars *a*, muffle *b*, and roasting pan *c*. The crucible smelting furnace *g* is shown with grate bars *h*, ash-pit *i*, and crucible *k*. The position given the crucible is probably a trifle higher than it should be above the flue *l*. The cover *m* is seen in section above the furnace. Bullion furnaces are designed to receive a No. 125 Dixon plumbago crucible, which has a capacity of 4.875 gallons, or 1,126⅛ cubic inches.

CHEMICALS NECESSARY FOR BARREL CHLORINATION

49. Charging the Barrel.—The chemicals used in the barrel process for dissolving the gold are bleaching powder and sulphuric acid. The sulphuric acid is placed in the water in the barrel before the ore is added. After the ore is run in the bleaching powder is added. The amount of acid and bleaching powder to be used depends on the character of the ore. If there is nothing in the ore to unite with the chlorine except the gold, the amount of chlorine consumed by the gold is extremely small. To convert 1 ounce of gold into trichloride of gold requires .64 ounce of chlorine.

50. Bleaching powder, also known as chloride of lime, should be of the best quality. It is made by passing chlorine gas through slaked lime and is assigned the chemical formula $Ca(ClO)_2 + CaCl_2$. It is considered a mixture of hypochlorite and chloride of lime. (See Art. 8.)

The amount of available chlorine contained in bleaching powder varies from 20 to 30 per cent. If bleaching powder is exposed to the air, it undergoes some change, losing part of its chlorine.

51. Calculating the Quantity of Bleaching Powder Required.—Solutions act more rapidly when saturated with chlorine. Under ordinary conditions of temperature and pressure, water dissolves about $2\frac{1}{3}$ volumes of the gas. The amount of water added to the barrel should, therefore, be sufficient for a saturated solution of the gas. If the barrel had a capacity of 160 cubic feet and the charge consisted of 600 gallons of water and 5 tons of ore, the space the water would occupy can be found as follows: $\frac{600 \times 231}{1,728} = 80.25$ cubic feet. Assuming 1 ton of ore to occupy a space of 10.75 cubic feet, the charge of 5 tons, together with the water, would occupy 134 cubic feet, thus leaving 25 cubic feet of space for air or free gas. The water will absorb $80.25 \times 2\frac{1}{3} = 187.25$ cubic feet of chlorine gas, and there will be 25 cubic feet in the air space. The specific gravity of chlorine gas being 2.45 compared with air, at 60° F. and 30 inches barometer, the weight of 212.25 cubic feet of chlorine gas can be found as follows: $w = \frac{1.3253 \times B}{459 + t}$ $= \frac{1.3253 \times 30}{459 + 60} = .0766$ as the weight of 1 cubic foot of air under the above conditions. Then, $212.25 \times .0766 \times 2.45 = 39.83$ pounds. This could be supplied by the decomposition of 132.76 pounds of bleaching powder carrying 30 per cent. chlorine gas.

52. Loss of Chlorine.—If the metallic oxides were not all expelled from the ore by roasting, they would absorb

chlorine. This may be ascertained by watching the pressure gauge on the barrel or testing for excess of chlorine from time to time, by means of a testing valve in the barrel and a little ammonia. In such cases, a second and maybe a third charge of chemicals will be required before the gold is dissolved by the chlorine water. The chances for loss if the ore is not properly roasted and chlorinated are here observed to be twofold, since there is a loss from excessive use of chemicals, and the percentage of gold extracted will be less. In some instances, where ore has not been properly roasted, it has been necessary to clean out the chlorinating barrel and reroast the ore. Some consider that this gas should exert considerable pressure in the barrel—at least two atmospheres. The percentage of extraction obtained by the Plattner process was as great as by the Theis process, where two atmospheres (29.4 pounds) was considered about the proper pressure. Those who advocate considerable pressure in the barrel neglect the fact that cold chlorine gas is more readily absorbed by water than chlorine gas having a temperature above 104° F.

53. Quantity of Bleaching Powder Required in Practice.—Theoretically, 7 parts of chloride of lime require 6 parts of sulphuric acid for complete decomposition. In practice, an excess of acid is added to prevent any lead or lime going into the solution as chloride, as they would consume chloride. The acid, also, when in excess would dissolve any metallic oxides that might be present in the charge. The relative amounts of chemicals used in practice are 6 parts of bleaching powder to 7 parts of 66° B. commercial sulphuric acid. In practice, 12 pounds of chloride of lime containing 30 per cent. available chlorine and 15 pounds of sulphuric acid are added to each ton of ore.

DETAILS OF THE BARREL PROCESS

54. Quantity of Water to be Used.—When charging a chlorination barrel, water is first introduced through the manhole until it reaches a certain mark. The amount of

water varies with the ore. The quantity usually required is from 80 to 120 gallons per ton of ore. This will make an easy-flowing pulp. If too little water is used, lumps are formed, which are not broken, and these lumps are imperfectly chlorinated. The sulphuric acid is next added, the required quantity having been previously determined in the preliminary experiments. The ore is brought to the barrel by a chute from an overhead hopper. It is convenient to have the hopper hold the exact quantity of ore for charging the barrel. The bleaching powder is added to the barrel last.

55. Revolving the Barrel.—The barrel is revolved for that period of time which was determined in the laboratory by experiments to be best adapted to the class of ore being treated. The physical condition of the gold determines the time more than any other one thing; consequently, more time must be allowed for coarse particles of gold than for fine.

The object of revolving the barrel is to agitate the pulp and bring the sulphuric acid into contact with the bleaching powder and so generate chlorine; then, again, the chlorine can permeate the pulp and come in contact with the gold to better advantage.

56. The barrel is usually revolved from 3 to 6 hours, during which time tests for chlorine gas are made to see if it is in excess. If free chlorine is not detected issuing from a test petcock when it is opened, the barrel is stopped opened and more bleaching powder and sulphuric acid added. Chlorine issuing through the petcock must be recognized by its odor and color, or else by the white fumes of ammonia chloride previously described.

Pressure of gas in the barrel does not always signify the presence of chlorine, because other gases besides could be generated in the barrel and issue through the petcock.

57. Leaching and Filtering.—When the chlorination is completed, that is, when all the gold possible has been leached from the ore, the barrel is stopped so that the filter

will be exactly horizontal. Connections are made with the pressure pump and settling tank and the liquor containing the gold drained off. Sometimes, water is forced into the barrel instead of air, the pressure not often being raised above 40 pounds per square inch. The water that enters the barrel, after absorbing the gas in the barrel, washes the tailings, and this washing is continued until tests made for gold show the wash water to contain none. At intervals, the leaching is suspended and the barrel revolved a few times so as to thoroughly mix the contents and prevent channels forming through the ore. It takes from 30 to 60 minutes to wash the ore.

58. When the leaching is complete, the ore is discharged into the sluice that leads to a settling tank. The barrel is next washed out with a hose, after which it is ready for another charge.

The tailings are sometimes discharged into a car and then run out to a tailings dump. The sluice, however, is the better means of disposing of the tailings, provided there is plenty of water at the mill.

59. Settling Tanks.—The filtered trichloride-of-gold solution as it comes from the barrel contains more or less sediment or solid matter in suspension. If this were permitted to go into the precipitating tanks, it would interfere with the complete precipitation of the gold and also make a poor bullion. There would also be time lost in allowing the precipitates to settle, unless something was added to the solution, a rather dangerous proceeding, since further debasement of the bullion would occur. It is, therefore, to the advantage of the process to provide settling tanks into which the trichloride-of-gold solution is discharged from the chlorination barrel.

The settling tanks are so arranged that the overflow from one passes into the next one situated on a lower level. After the solution has become free from suspended matter it is pumped into the precipitating tanks.

60. Precipitating Tanks.—The precipitating tanks are elevated above the pressure tank and the filter press, so as to obtain a gravity fall and avoid use of power when filtering the liquor. The outlet for the precipitating tanks is about 4 inches above their bottoms, in order to allow the precipitate to accumulate from three or four precipitations. Were the precipitates run directly to the filter press after each precipitation, there would be power lost and other expenses for material and labor which can be saved by filtering the precipitates from several operations together. The nearly clear liquor remaining after the precipitates have settled is run from the upper tank to the lower and allowed to stand for awhile or until the upper tank is required again. The liquor is then allowed to run by gravity through the filter press, where any gold sediment will be caught on the filter cloth.

The settling tank for the precipitates is not always required, but it may be advisable to use it on special occasions and so save time.

61. Eliminating an Excess of Chlorine.—When the precipitating tank has been filled with trichloride-of-gold solution to within 1 foot of the top, the free chlorine is to be gotten rid of, otherwise it might convert some of the gold precipitated back into trichloride or aurous chloride. To eliminate the chlorine, sulphur dioxide is passed through the solution. A sulphur-dioxide generator is shown at *a*, Fig. 12, so arranged as to deliver the gas generated through pipe *b* into the tank *C* and allow it to escape into the liquor through the perforated pipe *d* above the bottom outlet *e* of the tank.

To produce the sulphur dioxide, from 5 to 10 pounds of lump sulphur is inserted through the manhole *f* on to the iron pan *g*. The plug cock *i* is opened, while cocks *j* and *k* are closed, in order that the gas shall pass through pipe *b*. The sulphur having been ignited and the manhole closed, the compressed air is admitted through cock *h* into the bottom of the generator. This furnishes air for combustion and sufficient force to drive the sulphur dioxide out of the pipe *d*.

62. The free chlorine in the solution is rapidly converted into hydrochloric and sulphuric acid in accordance with this equation:

$$2Cl + SO_2 + 2H_2O = H_2SO_4 + 2HCl$$

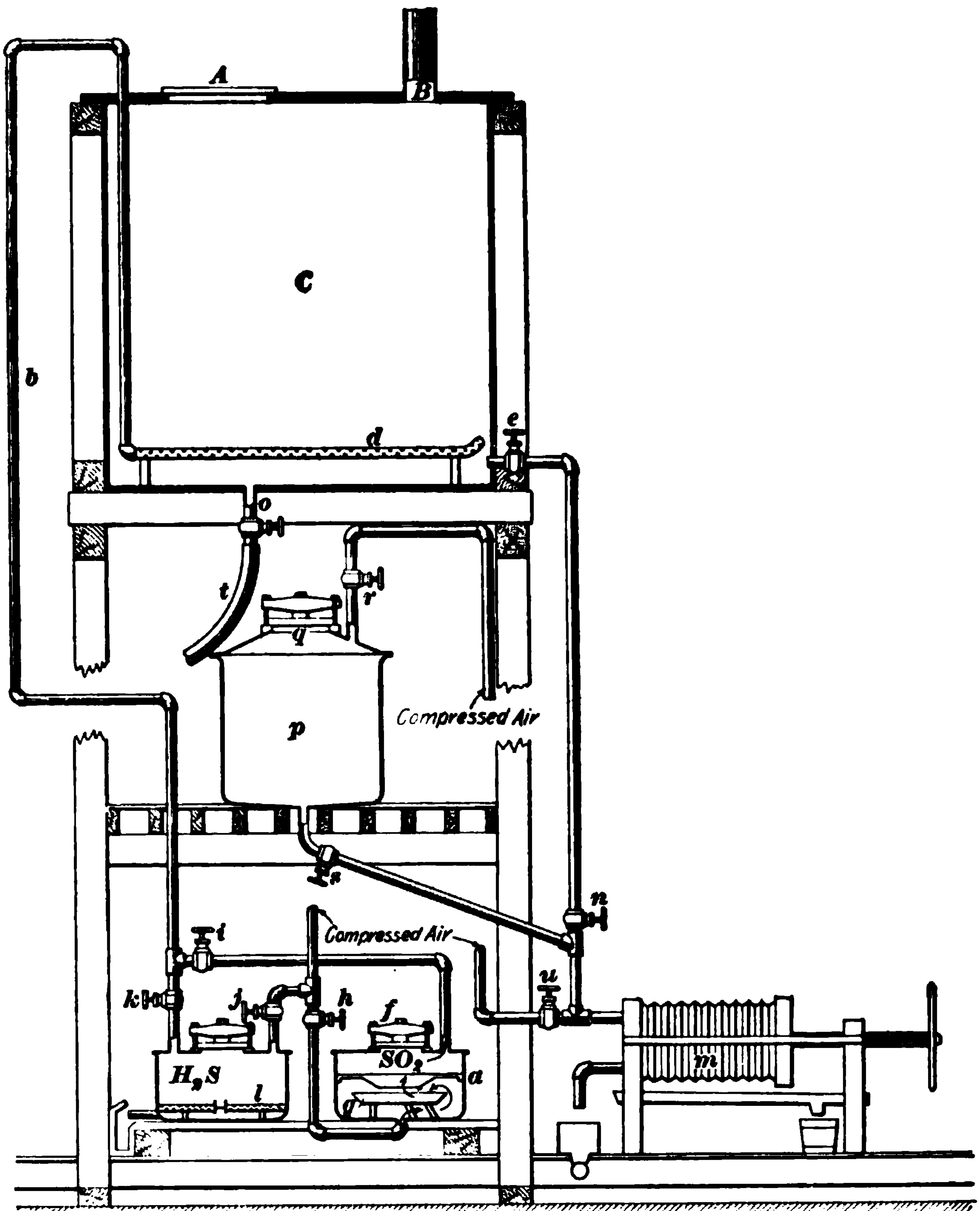


FIG. 12

The solution changes during the operation from a light yellow color to a clear, water-looking solution. The operation

takes from 15 to 20 minutes, but its completion should be tested by taking a beaker full of the solution and testing it with hydrogen-sulphide gas. If a permanent precipitation of gold immediately takes place, sufficient sulphur dioxide has been passed through the tank. On the other hand, should the precipitate formed disappear upon stirring the solution with a clean glass rod, more sulphur dioxide must be passed through the tank solution. Some consider it good policy to pass an excess of sulphur dioxide through the tank solution, while others think the chances for loss of gold are about the same for too much as for not quite enough sulphur dioxide.

63. Throwing Down the Gold.—To precipitate the gold from solution in tank *C*, Fig. 12, a hydrogen-sulphide generator *l* is attached to pipe *b*. The generator is charged through the manhole in the top with iron sulphide and water, the sulphuric acid is admitted through the acid chamber *e*, Fig. 7. The plug cocks *h* and *i* are closed and *j* and *k* opened, in order to direct the compressed air and the hydrogen sulphide in the proper direction.

The gold precipitated by hydrogen sulphide quickly settles, usually in about 2 hours, so that the clear liquor may be drawn off through valve *e* into the filter press *m*, while the precipitates remain in the bottom of the tank below the outlet *e*. This process of decantation and filtration requires 3 or 4 hours, which time may be greatly reduced by running the solution into a settling tank and feeding the press from that tank. When the solution has run down, valves *e* and *n* are closed and the precipitating tank refilled with gold solution.

64. The Pressure Tank.—When the accumulated precipitates from several operations are to be cleaned out of tank *C*, they are washed through the pipe *o* into the pressure tank *p*. The pressure tank is provided with a manhole cover *q*; by valve *r* it is connected with an air-compressor pipe and by valve *s* with the pipe leading to the filter press.

The 4 inches of precipitates are washed into tank *p* through

a rubber hose *t* attached to discharge pipe and valve *o* The manhole *q* is closed, then the valves *n* and *u*, after which valves *r* and *s* are opened. The compressed air coming through valve *r* presses the solution into the filter press *m*, where it eventually becomes a caked mass of gold and sulphur.

65. The sulphide cakes and the cloths are collected in an iron pan 44 inches long, 24 inches wide, and 4 inches deep, made of No. 8 iron. The pan, when charged with the sulphide, is placed in the muffle furnace, where the sulphur is volatilized and the cloths reduced to ashes. If the solutions were clear in the precipitating tanks, the roasted precipitate will have a light yellowish-brown color and should assay from 75 to 80 per cent. gold.

REFINING THE GOLD

66. Fluxing the Sulphides.—When sufficiently roasted, the residues are carefully mixed with a little borax, soda, and niter. Sometimes the leaching solution is not clear and contains a perceptible amount of slimes (ore), which accumulated with the sulphides in the precipitating tank; or the precipitate of sulphides may contain considerable quantities of arsenic and antimony, which were dissolved during chlorination, then precipitated by the sulphur dioxide, SO_2, or by hydrogen sulphide, H_2S, and have not been subsequently eliminated by roasting. All these conditions have to be considered and the necessary fluxes added to secure a fusible slag (that is, a liquid slag that will pour clear).

If the residues are silicious, alkaline flux, such as soda, potash, etc., will be required. If the residues are basic, silicious flux, such as glass, sand, etc., must be added. If sulphur, arsenic, or antimony has remained, niter or metallic iron may be added. Only general rules of fluxing can be given. The metallurgist in charge will be compelled to determine the proper fluxes necessary. A little experience will soon teach one what flux will give the purest bullion.

67. Melting the Precipitate.—The roasted precipitate is handled as little as possible. It is weighed in the pan and the weight of the pan deducted. The fluxes, as given in another place, are carefully mixed with the precipitate and the whole transferred to plumbago crucibles, melted, and when fluid poured into a conical mold. After the bullion is cold, it is cleaned of adhering slag, remelted with a little borax glass, and cast into a bar.

The mold should be coated with tallow or chalk and warmed, so that there will be no difficulty in removing the ingot when cold. The metal when poured should be just a little hotter than its melting point. A little slag should be run in the bottom of the mold first, as this will insure a smooth, homogeneous ingot. When both the metal and the mold are too hot, the resulting ingot is full of blowholes, and it then becomes difficult to sample correctly.

68. Refining the Slag.—The slag may contain a small amount of gold. It is therefore crushed to about $\frac{1}{8}$ inch in size. Then 7 pounds of slag are mixed with 1 pound litharge and melted in a crucible, the resulting lead is cupeled or it can be sold to the smelter.

SCOPE OF THE PROCESS

69. Chlorination may be practiced on ores that contain easily volatilized impurities and gold enough to warrant. The extraction in some instances reaches as high as 98 per cent. of the gold in the ore; again, in another locality it may not exceed 85 per cent. These factors are of vital importance; for instance, if one is treating a $10 ore and the cost of treatment is $9, in one case he would make 80 cents per ton and in the other lose 50 cents.

The same reasoning will extend to other factors which enter into the cost of chlorination; for instance, if there was a margin of profit, provided fuel cost but $2 per ton of ore, that profit would probably be wiped out when fuel cost $3 per ton of ore roasted.

70. From what has been said above, it becomes self-evident that the process cannot be applied to very low-grade ores unless they do not require roasting. The factors which determine the lowest grade of refractory ore which can be treated by the chlorination process are cost of fuel, cost of labor, cost of chemicals, and whether a dead roast is required for a given extraction which will show a profit. If the percentage of extraction enters into the cost of treatment, this should be carefully determined by experiment before erecting a mill, especially if the margin is close and the extraction involved is high.

COPPER SMELTING AND REFINING

COPPER ORES

1. Copper Sulphides.—The most abundant and important ores of copper are the sulphides, native copper, and the carbonates. Of the sulphides, chalcopyrite, $CuFeS_2$, probably supplies the greatest quantity of the metal. There are large deposits of pyrite, FeS_2, that contain a sufficient quantity of chalcopyrite to be important copper ores. Chalcocite, Cu_2S, is also important, and bornite, or purple copper, Cu_3FeS_3, occurs to some extent. Tetrahedrite, or gray copper, and enargite, which are of quite variable composition, usually occur only in small quantities, and fortunately so, because the antimony and arsenic which they contain are difficult to get rid of and injure the copper for most uses.

2. Native Copper.—After the sulphides, the next most important source of copper is the native copper of the Lake Superior district in Michigan. Native copper is such as occurs in the mine in the metallic state and not chemically combined with any other element, such as sulphur or oxygen. Native copper is found in small quantities in other places, but it is generally of less importance than some of the other copper minerals. At Lake Superior, however, it forms the entire copper supply.

3. Copper Oxides and Carbonates.—The mines of Arizona are at present the chief source of the oxide and carbonate ores of copper. There are two carbonates, **malachite,** $2CuO + CO_2 + H_2O$, which is green, and **azurite,** $3CuO + 2CO_2 + H_2O$, which is blue. The red oxide, **cuprite,** Cu_2O, is of some importance, but the black oxide, **melaconite,** CuO, seldom occurs in any considerable quantity.

CLASSIFICATION OF COPPER EXTRACTION PROCESSES

4. Most of the world's copper is extracted from its ores by **smelting.** Smelting consists in a series of operations conducted with ores at a melting temperature in suitable furnaces. This produces various chemical changes that finally result in the separation and concentration of the metal from the other constituents of the ore. For some low-grade ores, leaching processes are used; that is, the copper is dissolved by water, acid, or other solvent; the liquor resulting is then drained from the ore and the metal is finally precipitated from the solution by suitable reagents.

An ore containing as much as 6 or 8 per cent. of copper would probably always be smelted (and even poorer ores than this are smelted) either directly or after mechanical concentration. With ores that contain much vein rock, that is, quartz, feldspar, calcite, etc., it is generally cheaper to remove most of the gangue from the copper mineral by mechanical concentration than to smelt direct. Leaching processes are applied to certain ores that contain 4 per cent. or less of copper. The ores of Lake Superior contain from .5 per cent. to possibly 5 per cent. of native copper; but in this case the valuable mineral is so heavy that it can advantageously be concentrated by the aid of water into a product averaging about 80 per cent. of copper, which is smelted.

SMELTING PROCESSES

5. Copper ores are smelted either in blast or reverberatory furnaces. In the former the ore is mixed with the fuel required to produce the necessary heat, and the fuel is burned by blowing air through the mass. In reverberatory smelting, on the other hand, the ore and fuel are kept separate, and the ore is melted by the hot gases that pass over it from the fire. A blast furnace is fed and discharged continuously, but a reverberatory furnace has one charge withdrawn before another is introduced. The two methods can best be compared after each has been described in detail.

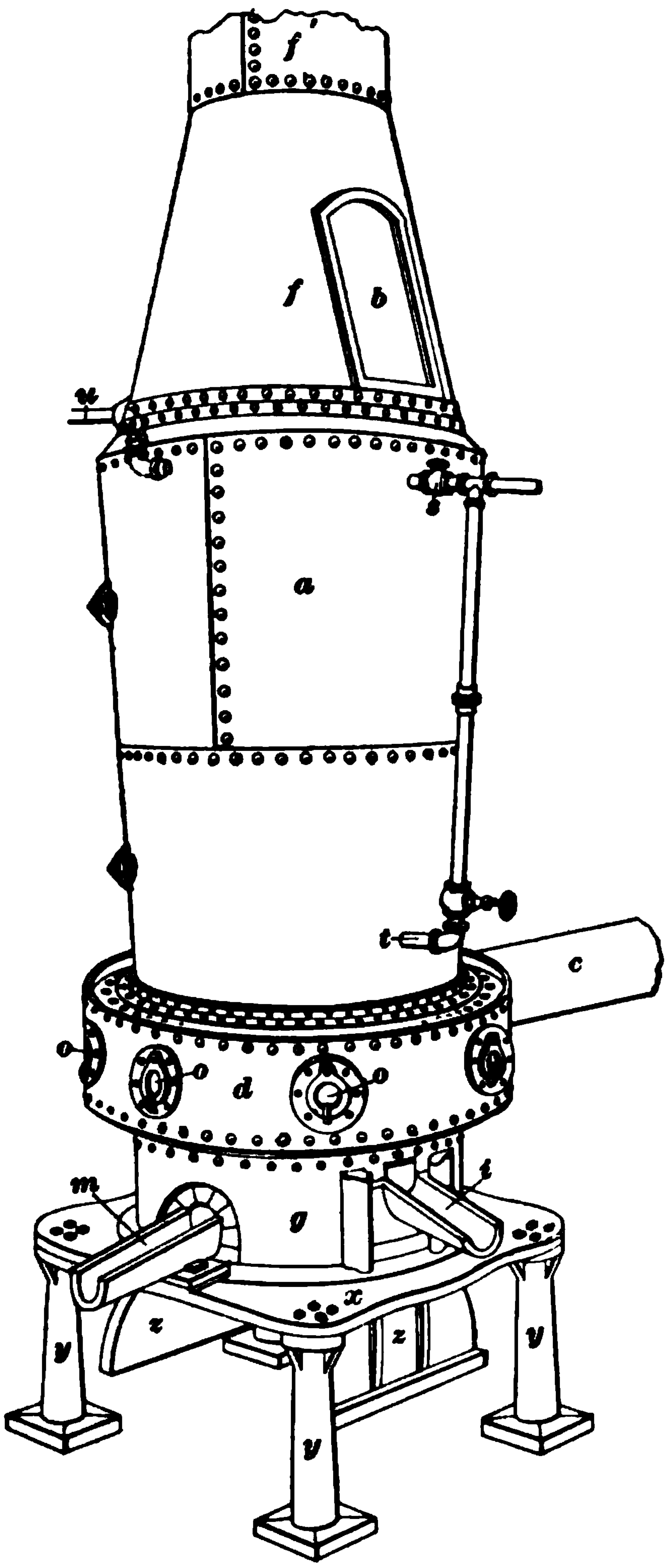


FIG. 1

THE BLAST FURNACE

6. General Description of a Blast Furnace.—A perspective view of a small copper blast furnace is shown in Fig. 1. It consists of inner and outer wrought-iron or steel shells *a*, which rest upon a cast-iron plate *x*; this is in turn supported by cast-iron

legs *y*. The whole stack between the base plate *x*, the hood *f*, and the stack *f'* form a hollow cylinder for the reception of ore, flux, and fuel. Water enters between the two shells through the pipes *s* and *t*, though usually at *s*, and after becoming heated, flows out at *u*. The object of this water is to reduce the temperature sufficiently to prevent the inner shell from burning out. Air enters the furnace through the pipe *c* into the wind box *d*. The object of forcing air into the furnace is to supply oxygen for the combustion which must go on during smelting operations. At *o* there is a piece of mica, through which the furnaceman looks from time to time to ascertain under what conditions the smelting is taking place. The spout *m* is for copper or matte, and the spout *i* for slag to flow from the furnace. The door *b* is for the purpose of charging the furnace with the necessary materials for smelting. The height of small furnaces between the tuyeres at *o* and the door *b* is about 5 feet, but for large furnaces the height sometimes reaches 10 feet. Just below the door of the furnace a floor is arranged for the charger to stand upon; this is not shown in the figure. Below the crucible *g* of this furnace there are two hinged doors *z*, shown opened, but which are held in position by a screw jack when the furnace is in working order.

7. Fig. 2, which is a vertical section of the furnace shown in Fig. 1, gives further details of its construction. The inner plates *p* and the outer plates *r* are shown with water between them, thus forming what is termed a **water-jacketed** furnace. From the wind box *c*, pipes *e* are seen extending into the furnace; these are **tuyeres**, through which the air blast passes. The peep holes *o* in the wind box permit the furnaceman to look through the wind box and tuyere into the furnace. In case the furnace tuyere becomes clogged, a bar is inserted through the hole *o* and the obstruction removed.

8. When a furnace works properly, the smelting occurs just above the level of the tuyeres, and this location is

termed the **zone of fusion.** Above this a large body of solid material absorbs the heat, and by the time it reaches the zone of fusion, it is in a proper condition to be quickly liquated. The hot fused material settles into the crucible *g* and is drawn off through openings *h* and *k*.

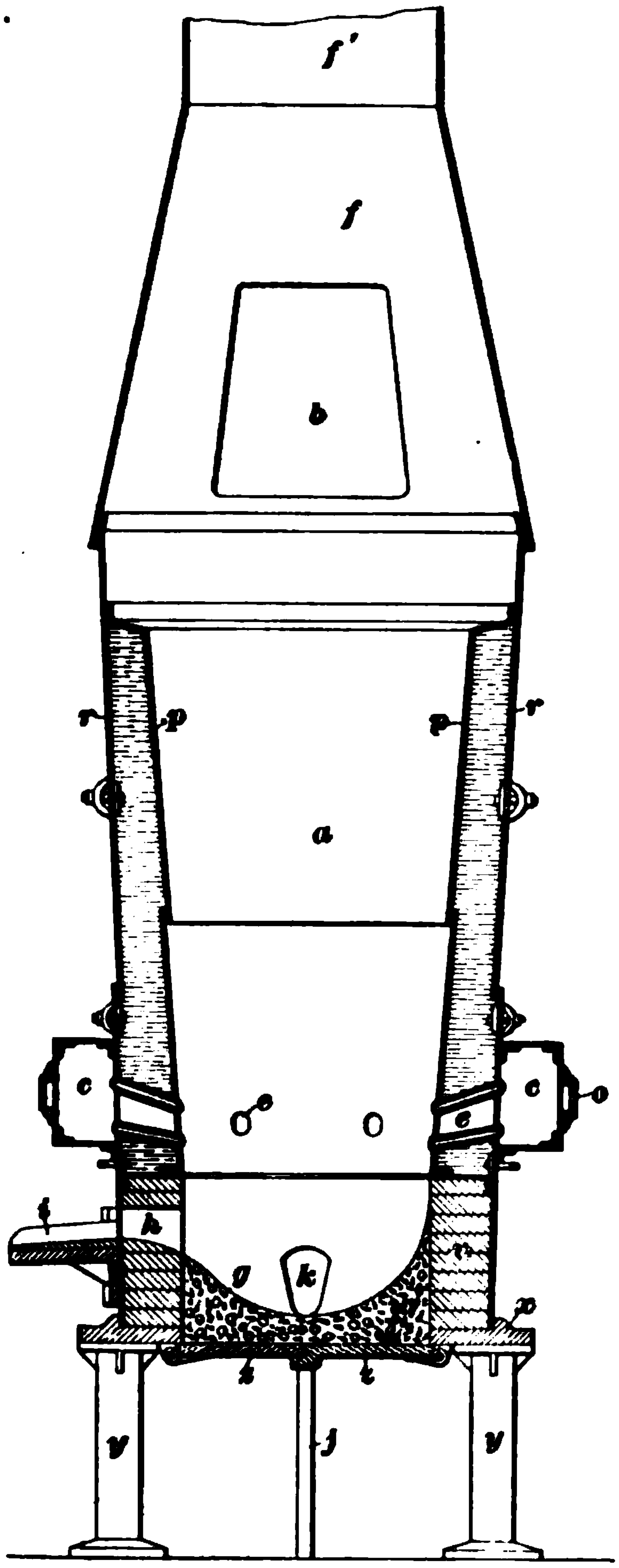


FIG. 2

9. The crucible *g*, which holds the molten material, is lined with firebricks *v*. Upon these firebricks the water-jacket rests. The bottom of the crucible is lined with a mixture of powdered fireclay and coke, which is tamped solid and then scooped out to form the shape shown by *w*. This lining, which is termed **brasque,** rests upon the hinged plates *z*, which are shown supported in place by the jack, or prop, *j*. When it is desired to remove the worn-out brasque, the doors *z* are dropped.

The crucible is one of the vital points of a smelting furnace and must not be allowed to chill or become filled with thick molten material that will not run from the spouts. In the furnace just described the matter is not so important, but in large furnaces, where much time will be lost in removing obstructions of this character, the matter is serious.

PRACTICAL HINTS TO SMELTING PRACTICE

10. Objects to be Achieved.—Blast-furnace work consists in melting ores by means of fuel and fluxes. Most ores are difficult to fuse alone and do not furnish fluid slag enough to allow of quick, thorough concentration. For this reason, if the ore is basic, an acid flux, such as silica, is added; or, on the other hand, if the ore is acid, a basic flux, such as limestone, is added. The charge for a blast furnace consists of definite proportions of the three ingredients—fuel, ore, and flux. The elements of the charge should be so proportioned that there will be obtained the highest concentration with the least consumption of fuel and flux, a matter which can only be attained by close attention to the chemical constituents of the elements entering into the charge.

11. Objections to Fine Ore. — Copper ores that have been mechanically concentrated or are finely pulverized cause considerable trouble in a blast furnace by creating flue dust, choking the blast and **scaffolding,** that is, sticking to the sides of the furnace. Even when mixed with large proportions of coarse ore, fine ore smelts unsatisfactorily, and hence it is that reverberatory furnaces are employed to concentrate such ores.

12. Air Blast.—When a furnace is in operation, air is forced into it as noted, and for this purpose it is necessary to use blowers or air compressors. The force of the air blast must be such that it will extend half way through the charge, otherwise there would be a mass of unfused material in the center line of the furnace. If the diameter of the furnace is increased beyond 36 inches, so strong a blast is required that combustion is quickened, the heat extends upwards above the proper zone of fusion, and smelting commences near the upper part of the furnace, producing what is known as **hot top.**

Besides the change from the proper zone of fusion, increased blast causes considerable fine ore to be carried into the flues. Again, if silver or gold be present, they are liable to be carried over into the flues by the strong blast,

especially if they exist in a fine subdivision of particles. The precious metals are almost sure to be carried from the furnace as fumes, if zinc, arsenic, or telluride be present in the ore. Fine particles of fuel are also carried over into the flues, if the blast is too great.

13. Inconvenience of Hot Tops.—Another disadvantage of hot top is the incomplete combustion of fuel at the top of the furnace and the consequent loss, together with the danger of an explosion from the carbon monoxide generated. To avoid the troubles mentioned, the widths of the furnaces have not been materially increased, but they have been changed from a circular to a rectangular shape. The length of the furnace furnishes area for increased capacity, instead of height and diameter, as in the case of iron blast furnaces.

14. Brick Versus Water-Jacket Furnaces. — Years ago the entire furnace was enclosed in brick walls, and such furnaces are occasionally used now. They have the disadvantage, however, that the melting ore chemically attacks the bricks and so gradually eats them away. Infusible parts of the ore often stick to the sides of the furnace and have to be removed by a bar pushed down from the feed opening, and the brickwork is apt to be more or less injured while removing such obstructions. The trouble is not confined merely to the repairs made necessary by the wearing away of the bricks, but the change in the dimensions and form of the furnace is likely to seriously affect the smelting process. The latter result is due to variations in the direction and velocity of the air-currents and to irregular settling of the ore charge. With water-jackets, there is neither chemical erosion of the walls by the ore nor mechanical erosion by barring off accretions. The large rectangular furnaces, such as shown in Fig. 3, generally have the upper part of the walls made of brick. This is because the difficulties just mentioned do not extend up to that part. Brick construction is cheaper where it can be used to a considerable

extent without leading to these difficulties. The brickwork does not bear on the water-jackets, as shown in Fig. 4,

FIG. 8

but is supported on the cast-iron pillars *a*, by means of the heavy I beams and angle irons *b* and *c*. The shape of the hood *o*, shown in Fig. 4, and of the flues *p* and *r* is such that

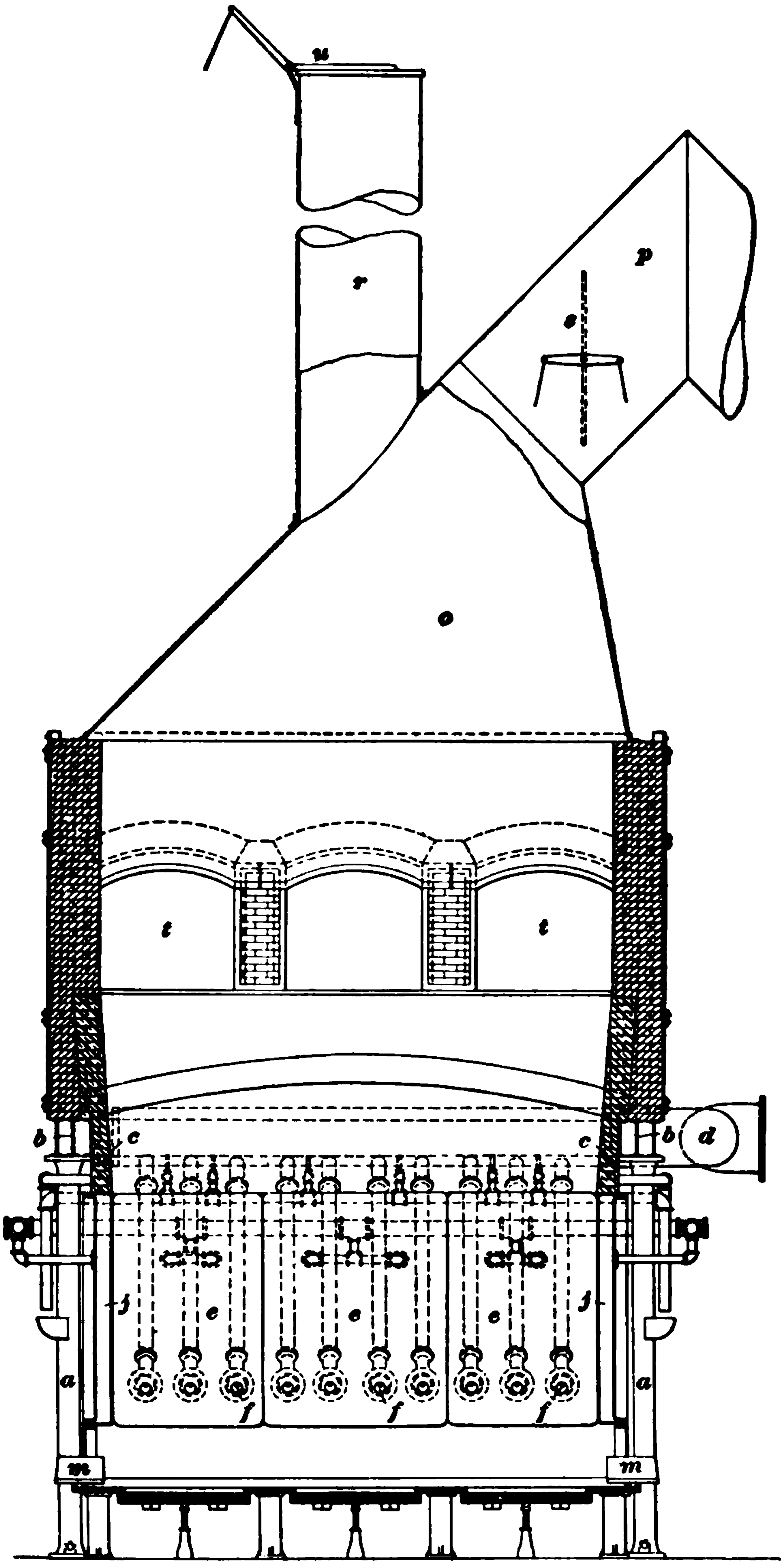


FIG. 4

brick construction would be difficult and expensive. They are therefore made of wrought iron.

15. Size and Shape of Furnace.—The reference just made to the large furnace shown in Fig. 4 brings up the question of size and shape. For small furnaces, the circular form, such as shown in Fig. 1, is the cheapest and most convenient; but when it is desired to very much increase the quantity of ore treated in a day, the diameter of such a furnace has to be so great at the tuyere level that the air will not penetrate to the center unless it is introduced with unusually high pressure. This high pressure would cause trouble in three ways: *First*, the strong blast would blow most of the fine ore out of the furnace. *Second*, the extremely rapid combustion of the fuel would generate such an intense heat that considerable metallic iron would be reduced from the ore. Some of this iron would separate in solid condition and clog the furnace. Such obstructions are called **sows**. *Third*, the fuel would burn in the upper part of the charge, and the cold air not finding any fuel near the tuyeres would chill the already fused material, so that it would not run properly.

To get a large capacity and at the same time avoid these difficulties, the horizontal section at the tuyere level is enlarged in one direction but kept comparatively narrow at right angles to that direction. Figs. 3, 4, and 5 show an oblong furnace 44 inches wide and 168 inches long, inside, at the level of the tuyeres. Furnaces are sometimes built wider than this; but it is generally found unwise to exceed a width of 48 inches, and 42 inches is perhaps the most common width. These large furnaces are sometimes built in the shape of an ellipse, as is shown in Fig. 6.

16. Furnace Bosh.—Above the tuyeres the furnace broadens towards the top, and these sloping sides are termed the **bosh**. This is more noticeable in Fig. 5, and where the width reaches its maximum enlargement, as at *w*, it is called

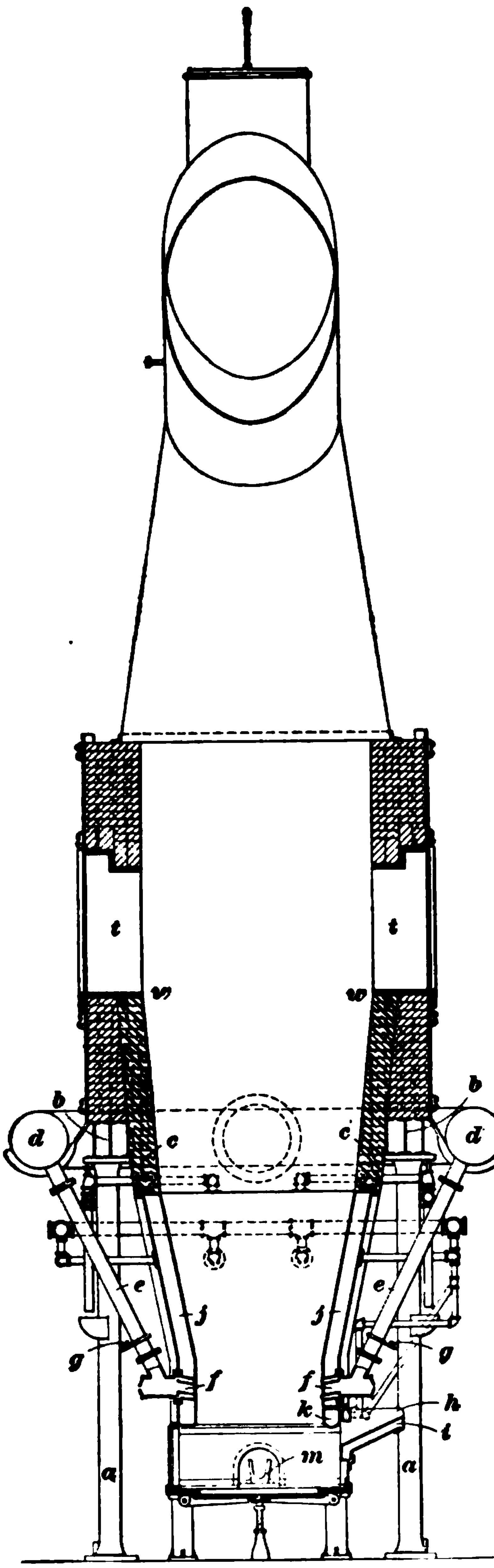


FIG. 5

the width of the **bosh.** The object of the bosh is to provide for gradual contraction in the charge, due to burning the fuel and fusing the ore, thus making the charge settle regularly, and the furnace work smoothly. Again the hot gases rising from the tuyere zone spread out over a wider area, which decreases their velocity so that their heat is more effectually absorbed by the ore.

17. Water-Jackets.—The jackets *j* are made of wrought iron, steel, cast iron, and even copper. Steel jackets are more expensive than cast-iron ones, and are by some not considered as durable. Cast-iron jackets may be broken by rough usage or by variations of temperature, especially if the castings are not carefully made. When the smelter is located near a foundry that will recast the old jackets for a reasonable sum, it will probably be cheaper to use cast-iron than wrought-iron jackets. Copper and iron jackets

have proved unsatisfactory, the two metals forming a voltaic couple, which increases the corrosion of each. Copper jackets are said by some to better withstand the corrosive action of copper sulphate, ferric sulphuric, or

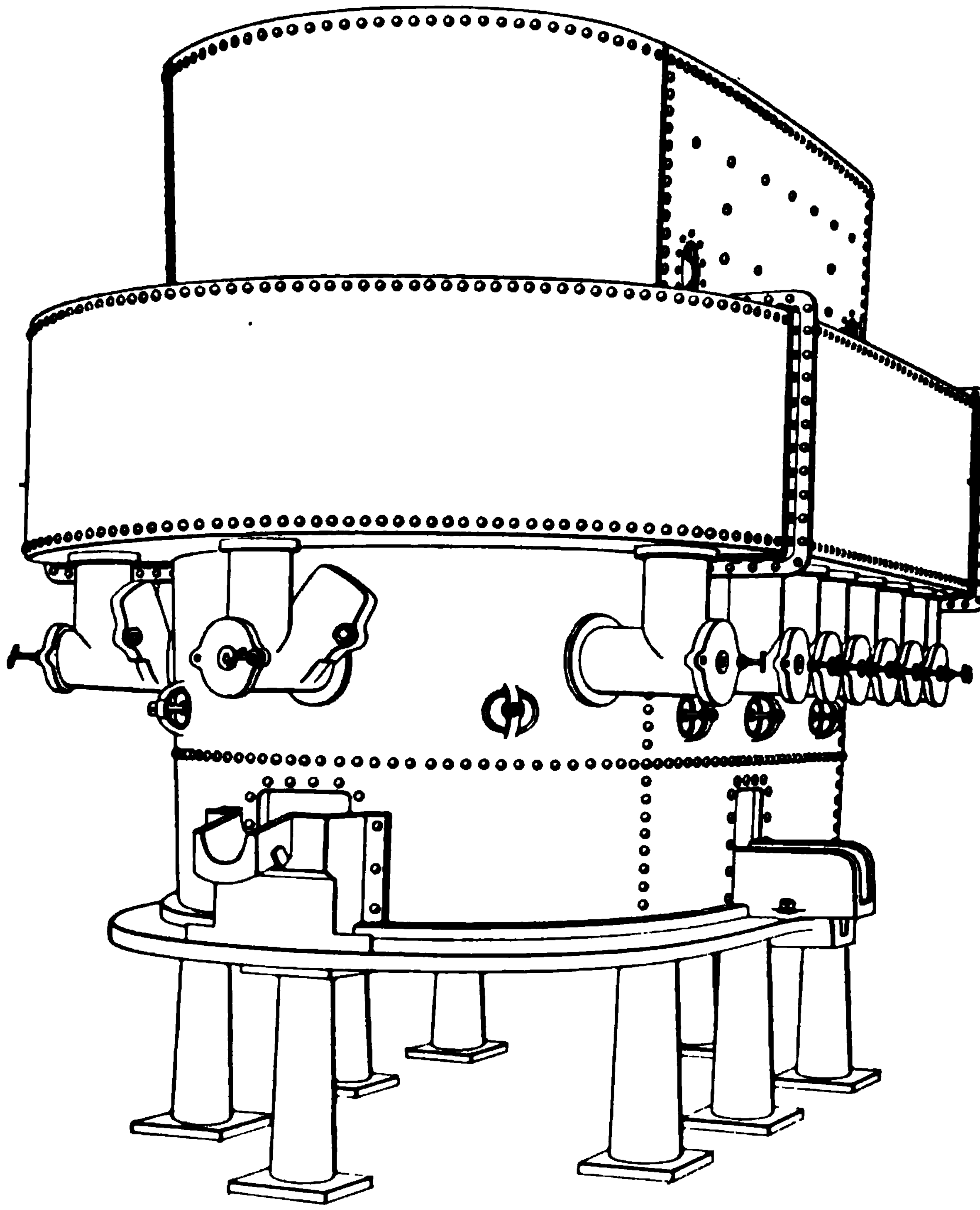


FIG. 6

sulphuric acid formed in the ore during roasting or exposure to the weather. Others claim there are no conditions in blast-furnace practice but are as well subserved by properly proportioned cast-iron jackets as by those of any other material.

18. Tuyeres.—In the furnace shown in Figs. 1 and 2, the air enters all the tuyeres directly from the wind box *c*; but in the large furnace, Fig. 3, the air is delivered from the blower into the bustle pipe *d*, from which it passes down through the individual tuyere pipes *e* on each long side of the furnace to the tuyeres *f*. Each tuyere pipe has a gate *g*, by means of which the amount of air can be regulated; or, if necessary, the air can be entirely shut off from any tuyere without affecting the others.

19. Flues.—As the waste gases are very much expanded by the heat and as considerable air is likely to be drawn in through the charging doors *t* by the draft, the main flue *p* is made very large. Its diameter is about 5 feet. The amount of air drawn in through *t* can be much reduced by adjusting the damper *s*, until no fumes come out of *t* when opened. The flue *p* leads to a central chimney that serves for several furnaces. If, on account of repairs or for any other reason, this flue cannot be used, the damper *s* is closed and the fumes are allowed to escape through the vertical flue *r* by opening the damper *u*, which fits over the top of stack *r*, as shown in Fig. 4.

OPERATION OF BLAST FURNACES

20. Definitions.—Copper blast furnaces may be run to produce either matte or metallic copper. For practical purposes, **matte** may be defined as a more or less complex artificial sulphide. A copper matte practically always contains iron as well as copper, and usually contains, also, small quantities of other metals. Any gold and silver in the ore pass into the matte; but, while they sometimes make up quite a large part of the value, they never constitute more than a small percentage by weight. The matte is apt to contain arsenic and antimony; but, if these are present to any great extent, they separate, in combination with some of the metal, as a product called **speiss.** The latter, however, is of very uncommon occurrence. In regard to the

valueless constituents of the ore, the object is to get them mostly into a waste product called **slag**. The slag is a silicate, produced by the chemical union of silica with the iron that does not pass into the matte or speiss, together with lime, alumina, etc. Lime is frequently added to the ore in the form of limestone, in order to help form a readily fusible slag, and because of this effect, it is called a **flux**, that is, something that makes the slag flow well. Manganese also goes into the slag, as well as part of the barium and zinc, if they are present. Part of the three latter metals may go into the matte and some of the zinc is volatilized. The sulphur goes partly into the matte, but a portion of it passes off into the flue as sulphur dioxide. Some of the latter gas may be converted into sulphur trioxide. Part of the sulphur contained in pyrite is distilled without being oxidized and may often be seen passing away from the top of the stack as a yellow cloud just after a fresh charge has been put into the furnace.

SMELTING FOR MATTE.

21. Sulphur for Matte.—As most copper blast furnaces are run to produce matte, the matting process will be described first and the production of metallic copper later. At the high temperature of a smelting furnace, copper has a greater affinity for sulphur than any other metal, so that copper in any other combination than sulphide will take sulphur from other metals. Then, the sulphur that remains, after satisfying all the copper, combines with other metals, especially iron, and the various sulphides unite to form the matte.

22. Copper in Matte.—If the ore contains a large amount of copper compared with the sulphur, it is smelted directly; but, if the sulphur is in excess, part of it is removed by roasting. The object of this roasting is to get rid of the large quantity of iron sulphide, which would dilute the matte and so make it poor in copper. The subsequent

treatment of very low-grade matte is troublesome and expensive. On the other hand, the matte must not be too rich, because a small quantity is always lost by failing to settle out of the slag. If this small quantity is of very high grade, the loss of copper will more than balance the decreased cost of the subsequent matte treatment. In American practice, the aim is generally to produce a matte containing from 45 to 55, or even 60, per cent. of copper.

The ore that is charged into a matting furnace generally consists of a mixture of raw sulphides, rich in copper, and of either roasted sulphides or carbonate ores.

23. Charging the Furnace.—The method of charging is to first put in the coke, with the ore and flux on top of the coke. *It is found that somewhat less coke is needed when comparatively large amounts of ore are charged at one time than when small amounts are used;* also, that it is easier to burn off sulphur in the furnace and thus make the matte richer in copper. In a round furnace 36 inches in diameter at the tuyeres, 500 to 800 pounds of ore and flux is a suitable quantity for a single charge; while for a 42" × 120" rectangular furnace, the charges weigh from 1 to 2 tons.

If the charge gets too hot in one part of the furnace, less fuel and more ore should be used there and the air supply may be temporarily shut off from that place. If one part is too cold, more of the fuel should be used there and some old slag substituted in place of the ore, because the slag requires less heat to melt than ore. Some suggest that the blast be reduced at the hot spot and charging continued as before, because of the rather difficult task of placing the material in a furnace just where one may wish.

24. Tapping Slag.—As matte usually has a specific gravity of about 5 and slag a specific gravity of only about 3.5, the former settles below the latter. When using the small furnace shown in Figs. 1 and 2, the slag is run out

through the spout *i* into a large iron pot mounted on wheels. This is done by driving a hole through the clay plug that closes the slag tap *h*, and when the slag has all run out, closing the hole again with a fresh plug. The matte is similarly discharged or tapped through the opening *k* and spout *m*. The slag must be tapped before enough has collected to run into the tuyeres *c* and the matte before it has collected sufficiently to reach the slag tap *h*.

25. Slag Overflow.—Slag sometimes overflows into the tuyeres, and if discovered in time, the accident may be remedied without causing much damage. To call the keeper's attention to troubles of this character, slag escapes have

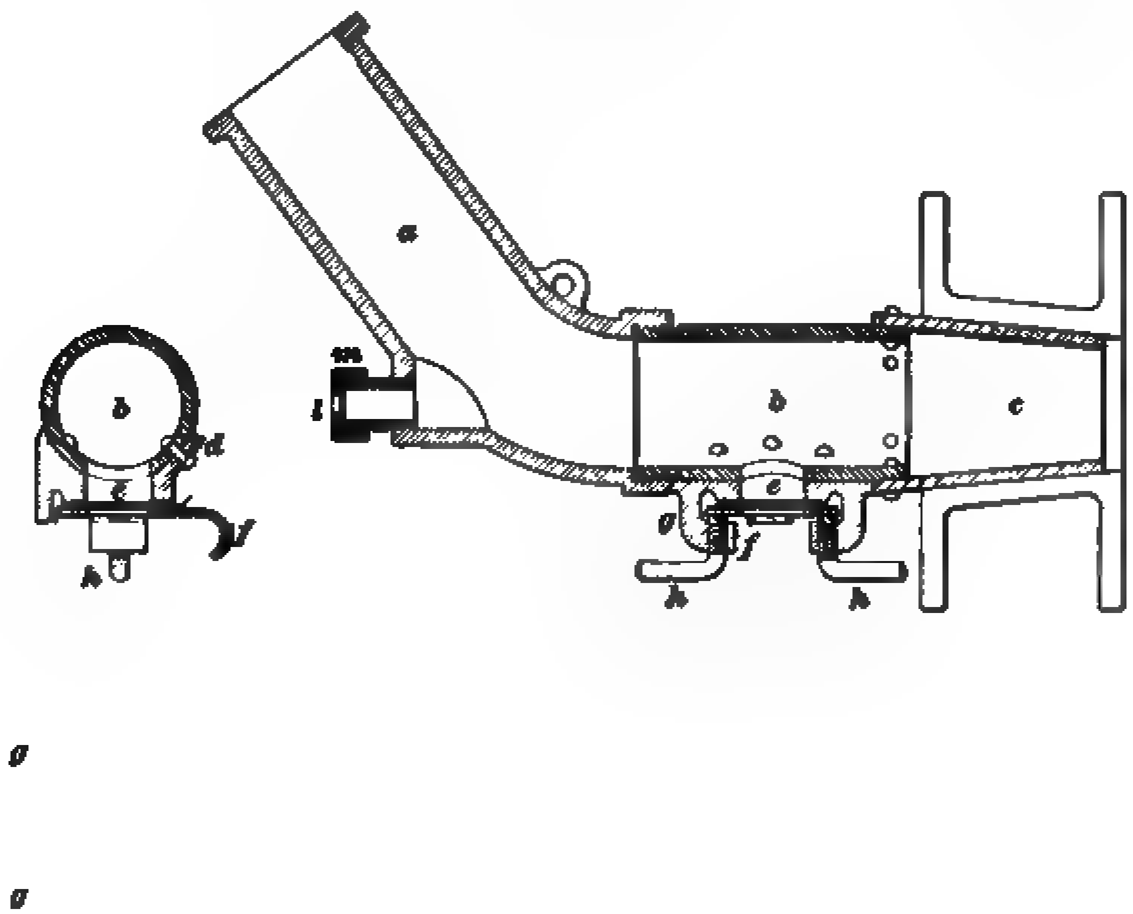


FIG. 7

been devised; that shown in Fig. 7 is known as the **Davis**. It is composed of three parts *a*, *b*, and *c*. To the under side of *b*, a perforated flange *g* is fastened. Through *b*,

f, and *g* there are holes, which are covered by a piece of oiled paper or linen *e*. The linen is held in place against *g* by a plate *f*, which in turn is forced up against *g* by the screws *h*, thus making an air-tight joint. In case the slag overflows from the furnace, the diaphragm *e* is burned out and air will escape with so loud a noise the furnaceman's attention will be called to the necessity of tapping the furnace.

26. Forehearths.—With the large furnace, Fig. 3, the slag and matte run out together continuously through the water-jacketed spout *h* and separate in a large forehearth or settler. These forehearths will be described later. The object of removing the products from the furnace as soon as formed is to prevent the possible accumulation of any unfused material, which would gradually choke the furnace. This method cannot be used with small furnaces, because the small quantity of matte and slag produced by such a furnace would rapidly solidify or "freeze" when removed from its source of heat.

Air can never escape through the spout *h*, Fig. 5, because the lip *i* is several inches above the bottom of the tymp *k*, thus effectually trapping the air by means of a body of liquid slag and matte. The tap holes *m* are used only when **blowing out,** that is, completely emptying the furnace. They are then opened to remove the matte that remains below the spout *h*. The purpose of keeping this body of matte below the discharge spout is to protect the firebrick bottom from the corrosive action of slag. The brick bottom and lining of the crucible are not shown in the figure.

LEAD FURNACE SLAGS

27. Composition of Slag.—The relative percentages of silica, iron, lime, and alumina that go to form the slag are very important, because the specific gravity and fusibility vary greatly with the composition. A slag that is too heavy

will not separate well from the matte. A slag that contains too much silica requires an unusually high temperature to melt, which means the use of much extra fuel. This high temperature and excessive fuel are likely to cause the formation of the infusible iron sows, which may so clog the furnace as to compel a shut-down. Sometimes, when a furnace is running badly, the simplest remedy is to charge some old slag. Less heat is required to melt this than to form a similar slag from the various substances that compose it. This slag, especially if it contains much iron, furnishes the best kind of flux to combine with and melt infusible parts of the ore. There is always on hand a certain amount of slag that contains too much copper to be thrown away and would have to be returned to the furnace anyway. This copper is present chiefly in the form of fine particles of matte that have failed to settle out. Most of the slag, however, contains only from .3 per cent. or less to .8 per cent. copper. Occasionally, there are ores that contain the right proportions of silica and of bases to form an excellent slag; and sometimes silicious and basic ores are to be had in suitable proportions to make a good slag when mixed together. The ores are very apt, however, to contain too much silica, and in such cases limestone is added to supply a base, and with the iron present increase the fluidity of the slag.

28. Lead and Copper Slags Compared.—It has been found by experience that the composition of slag for copper-matte smelting does not have to be so carefully regulated to prevent losses as in lead smelting. Slags varying between the limits of about 25 per cent. and 40 per cent. of silica are said to have been successfully run. It should be understood, however, that with such wide variations in the slag there will be decided variations in the amount of fuel required, in the number of tons of ore smelted per day, in the quantity and quality of matte produced from a ton of ore, and in the care that has to be used to keep everything running smoothly. Experience has shown that usually the best satisfaction is given by slags that are within the limits of

30 per cent. and 38 per cent. silica; and at Anaconda mine, Butte, Montana, the best results were obtained when the silica was near 36 per cent. and the sum of the percentages of ferrous oxide and lime was about 54 per cent. Such substances as zinc and barium, which sometimes occur in considerable quantities in lead smelting, and which make the slag so infusible and heavy that it does not separate well from the matte, fortunately are not often found in copper ores.

29. Example for Calculating a Slag.—The following hypothetical example shows the method of calculating any desired slag. The materials taken are supposed to be proportioned as follows:

Selected raw ore.....	15% Cu,	20% Fe,	35% S,	25% SiO_2
Roasted concentrates	25% Cu,	35% Fe,	10% S,	12% SiO_2
Refinery slag........	50% Cu,	10% Fe,		25% SiO_2
Limestone................................				50% CaO

Assume that a matte with 50 per cent. copper is to be made and a slag with 35 per cent. silica, 40 per cent. ferrous oxide, and 15 per cent. calcium oxide.

It is common to figure only 90 per cent. of the total amount made up of the three substances just enumerated, the remaining 10 per cent. being left upon the assumption that it will be accounted for by the aluminum oxide, magnesium oxide, manganese oxide, barium oxide, zinc oxide, and whatever other similar compounds are likely to be present in the mixture.

30. Iron in the Matte.—Before calculating the slag, it is necessary to calculate the quantity of iron that will be taken up by the matte. For this purpose, the matte is assumed to be a mixture of Cu_2S and FeS. Using the atomic weights of copper, sulphur, and iron, it is found that a 50-per-cent. copper matte will require 12.5 per cent. sulphur to combine with the copper.

$$Cu_2 = 64 \times 2 = 128; \; S = 32;$$

then,
$$128 : 32 = 50 : 12.5\% \; S.$$

There remains $100 - (50 + 12.5) = 37.5$ per cent. FeS, the iron of which amounts to 23.9 per cent., obtained as follows: $Fe = 56$; $S = 32$; then, $56 + 32 = 88$, and $\frac{56 \times 100}{88} = 63.63\% \times 37.5\% = 23.9$ per cent. That is, the matte contains $\frac{23.9}{50} = 47.8$ per cent. as much iron as copper. If, now, the copper with its proportion of iron and all sulphur are set aside, there will be left iron, silica, and limestone to form slag. If there is more than enough sulphur to form a 50-per-cent. matte, it is to be remembered that some of the sulphur is burned off in the furnace. Continuing the calculations, the iron left may be found as follows:

Selected raw ore, $47.8 \times 15 = 7.17$ and $20 - 7.17 = 12.8\%$ Fe

Roasted concentrates, $47.8 \times 25 = 11.95$ and $35 - 11.95 = 23\%$ Fe

Refinery slag, $47.8 \times 50 = 23.9$ and $-23.9 + 10 = -13.9\%$ Fe

Reducing these last results to their equivalents of ferrous oxide:

Selected raw ore, $56 : 16 = 12.8 : 3.65$ and $3.65 + 12.8 = 16.5\%$ FeO

Roasted concentrates, $56 : 16 = 23 : 6.56$ and $6.56 + 23 = 29.6\%$ FeO

Refinery slag, $56 : 16 = -13.9 : -3.97$ and -3.97 added to $-13.9 = -17.9\%$ FeO

The ferrous oxide, silica, and limestone may now be tabulated for comparison for further calculations:

	FeO	SiO_2	CaO
Selected raw ore....	16.5%	25%	
Roasted concentrates	29.6%	12%	
Refinery slag.......	−17.9%	25%	
Limestone..........................			50%

31. The ferrous oxide to which the iron is equivalent is given because the iron is all converted into FeO before it enters the slag. Referring to Art. **29,** it will be seen that the proposed slag is to contain 35 per cent. SiO_2 and 40 per cent. FeO; hence, by a simple proportion, the amount of silica to slag the ferrous oxide may be obtained.

Selected raw ore, $8 : 7 = 16.5 : 14.4\%$ SiO_2 and $25 - 14.4 = 10.6\%$ excess SiO_2.

Roasted concentrates, $8 : 7 = 29.6 : 25.9\%$ SiO_2 and $12 - 25.9 = -13.9\%$, or 13.9% deficiency SiO_2.

As the raw ore contains an excess of 10.6 per cent. silica and the roasted ore a deficiency of 13.9 per cent. silica, it will be necessary to mix 131 pounds of raw ore with every 100 pounds of roasted ore to satisfy the proportion

$$10.6 : 13.9 = 100 : 131.$$

The 25 per cent. SiO_2 in the refinery slag requires $7 : 8 = 25 : 28.6$ per cent. FeO, but this material must be supplied from another source before making the matte; in other words, the addition of 13.9 per cent. Fe or its equivalent 17.9 per cent. FeO is necessary to make the desired slag. For matte and slag together, $28.6 + 17.9 = 46.5$ per cent. FeO is required and may be supplied from the roasted concentrates, which contain an excess of 15.9 per cent. FeO. Each 100 pounds of refinery slag will require, then, $15.9 : 46.5 = 100 : 292$ pounds of roasted concentrates.

32. Lime has not been provided for in either of the mixtures. As the slag is to contain, according to Art. **29,** 15 per cent. CaO and 35 per cent. SiO_2, or $\frac{15CaO}{35SiO_2} = \frac{3CaO}{7SiO_2} = \frac{3}{7}$ as much lime as silica, it becomes necessary to calculate the weight of silica in each mixture. In the raw and roasted ore mixture, 131 pounds of raw ore contains 32.8 pounds of SiO_2 and 100 pounds of roasted ore contains 12 pounds of SiO_2, a total of 44.8 pounds of SiO_2. The necessary amount

of CaO, then, is $\frac{3 \times 44.8}{7} = 19.2$ pounds. As the limestone contains but 50 per cent. CaO, twice this amount will give the required weight of limestone, or $19.2 \times 2 = 38.4$ pounds.

In the refinery slag, 100 pounds contains 25 pounds of SiO_2, and the 292 pounds of roasted concentrates contains 35 pounds of SiO_2, $(2.92 \times 12 = 35)$. The total is $25 + 35 = 60$ pounds of SiO_2 and the required amount of CaO is $\frac{3}{7} \times 60 \times 2 = 51.4$ pounds of limestone.

33. The above calculations summed up show two complete mixtures, each of which will yield the desired slag.

	First Mixture	Second Mixture
Raw ore...............	131 lb.	
Roasted concentrates...	100 lb.	292 lb.
Refinery slag..........		100 lb.
Limestone.............	38 lb.	51 lb.

As there is likely to be more raw ore than refinery slag at the furnace, the first mixture may be taken in double quantity while the second is taken as calculated. With this provision, the final mixture will be as shown in the column headed "Total Weight" in the following table. The rest of the figures in this table have been calculated as a check on the preceding calculations.

TABLE I

	Total Weight. Pounds	Cu Pounds	Fe Pounds	S Pounds	SiO_2 Pounds	CaO Pounds
Selected raw ore....	262	39	52	92	66	
Roasted concentrates	492	123	172	49	59	
Refinery slag.......	100	50	10		25	
Limestone.........	127					64
Total............	981	212	234	141	150	64

34. Considering simply the totals, the 212 pounds of *Cu* required 101 pounds of *Fe* for the formation of matte, and the remaining 133 pounds of *Fe* are equivalent to 171 pounds of *FeO*. This bears the same relation to the 150 pounds of SiO_2 and 64 pounds of *CaO* as does the 40 per cent. *FeO* to the 35 per cent. SiO_2, and 15 per cent. *CaO* in the desired slag, which indicates the accuracy of the calculations.

The 212 pounds of *Cu* and 101 pounds of *Fe* that go to form the matte require only 111 pounds of *S* to produce a matte with 50 per cent. *Cu*. The remaining 30 pounds of *S*, which is about $\frac{1}{5}$ of all the *S* in the charge, is converted into sulphur dioxide, partly by reducing ferric oxide, Fe_2O_3, to ferrous oxide, *FeO*, in the roasted concentrates and partly by direct oxidation.

35. The following figures show the slag analyses at a certain blast-furnace plant for six successive days.

TABLE II

SiO_2 er Cent.	*FeO* Per Cent.	*CaO* Per Cent.	Al_2O_3 Per Cent.
35.4	38.6	18.1	7.3
37.6	36.5	15.7	7.9
34.9	36 5	19.5	7.2
33.0	60.6		4.8
36.4	37.5	15.4	9.8
36.7	35.3	15.8	9.6

It is clear that the analysis varies more or less from day to day. This is because the materials in the charge are not altogether of uniform composition. On the fourth day no lime was used. A furnace will run properly without lime, but a slag containing a certain amount of it separates better from the matte. As little limestone should be used as is possible to obtain good results, because it requires fuel to melt

barren material; also, less ore can be treated in a day, besides the cost of limestone can thus be saved.

36. Handling Slag.—Fig. 8 shows one of the settlers or forehearths referred to in Art. **26** for receiving the matte and slag from a large blast furnace. The body of this forehearth is made of cast-iron plates *a*, *b*, *c*, held together by heavy bolts *d*, and has a lining of firebrick not shown in the figure. The furnace products discharge into the forehearth either at *e* or *f* and the slag overflows constantly from the upper spout *g*, while the matte is tapped periodically from the lower spout *h*. This settler is mounted on wheels, so that it can be quickly removed when repairs are needed and be replaced by a new settler, thus avoiding any serious delay in operating the blast furnace. Some of the largest settlers have a circular shape and can store up 5 to 10 tons of matte These are too large to be mounted on wheels, and when they need to be repaired, the blast furnace must be banked or blown out.

FIG. 8

In some instances, tilting forehearths have been introduced. These are arranged somewhat like a Leghorn converter, so that instead of tapping matte, as in the ordinary forehearth, the receptacle is tilted by means of a hydraulic piston until the slag has all run off. Further tilting discharges the matte. Where it is desired to store large quantities of liquid matte, a reverberatory furnace is used as a forehearth and a small fire is kept on the grate to prevent chilling.

37. Matte Settling in Slag Pot.—The slag overflowing from the forehearth, Fig. 8, runs into an unlined cast-iron

settling pot such as is shown in Fig. 9. Any matte that did not settle in the forehearth has another chance to settle here. The slag runs out from the spout *a* into a slag pot mounted on wheels and is carried away to the dump.

FIG. 9

Fig. 10 shows a slag pot holding about 400 pounds of slag used at small furnaces. At some of the large furnaces a pot of this size would be filled in 2 or 3 minutes, so that a very large force of men would be required to change the pots and wheel them away. For this reason, very much larger pots are used, one form of which, made by the Colorado Iron

FIG. 10

Works, is shown in Fig. 11. This will hold 4 or 5 tons of slag. It is moved to the dump by a small electric-motor engine, an endless rope, or a horse. Ordinarily, the pot is held in position by the hooks *a*. It is so balanced that it can be quite easily tipped over and emptied by hand. This is done by

means of the levers *b*, one at each end, each of which carries a dog *c*. This dog works against the teeth of the segmental casting *d*.

Fig. 11

After a pot is dumped there is a small amount of chilled slag sticking to the sides. This is always richer in copper than what was poured off, because of the matte it still contains, and it is generally returned to the blast furnace.

38. Location of Slag Dumps.—The slag dump should be as near the furnaces as possible, in order to save time and labor. There should be a slight grade from the furnaces to the edge of the dump, so that the full slag pots can be wheeled easily; but the grade must be so gentle that there will be no difficulty in wheeling back the empty pots. Care must be used, in emptying the pots, to keep the surface of the dump even and to maintain the grade. An illustration of slag dumping is given in Fig. 12.

39. Granulating Slag.—Sometimes, instead of removing the slag in pots, it is allowed to fall into a rapidly running stream of water. This quickly chills, granulates it, and then carries it wherever it is to be deposited. Care must be used to have plenty of water for this purpose, otherwise there will be such a sudden generation of steam as to

cause an explosion. In case molten metal comes in contact with the water, there is liable to be an explosion, which will cause hot material to fly in all directions. Persons have been seriously injured from this cause.

FIG. 19

40. Utilizing Slag.—The molten slag is sometimes made into bricks by casting it in iron molds. The bricks must cool slowly or they will be brittle. They are used for walls and for paving. Sometimes the slag is run into a bed of sand and when cold broken up for railroad ballast. Granulated slag may be utilized for filling. For this purpose it can be run into settling tanks together with the water used to granulate it, and be drawn out through a bottom gate as needed, or it can be removed continuously

from the tanks by bucket elevators. Granulated and crushed slag is sometimes used as a substitute for broken stone on roads.

41. Fuel.—The almost universal fuel used is coke, though charcoal, coal, and even wood have sometimes been substituted for part of the coke. In ordinary matte smelting, the quantity of coke used varies considerably, ranging from perhaps 8 to 18 per cent. of the combined weight of ore and flux. The quantity depends partly on the quality of the coke, a high percentage of ash decreasing its heating power. The coke should not be too dense or it will not burn fast enough. It should be strong enough not to crumble under the weight of the ore. If it does crumble, it will pack so as to burn with difficulty. A first-class coke suitable for iron smelting is not as desirable as a poorer or softer coke. The reason stated for this is that increased blast necessary for its combustion drives heat upwards and ignites the material above the zone of fusion, thereby creating a **hot top.** In places where there is likely to be a heavy fall of rain or snow, it is best to keep the coke supply under cover because the evaporation of water in the furnace absorbs heat to no purpose. The same remark applies to ore and fluxes.

42. Air Blast.—Figs. 13 and 14 show a Connersville cycloidal blower, which is driven by belt and pulley. One of the impellers *a* is connected with the shaft *c*, while the other impeller *b* is driven by spur gears enclosed in the gear casing *B*, Fig. 13. The impellers revolve in the directions shown by the arrows, and consequently the air is drawn in at *g* and discharged at *f*. The pressure is measured by a gauge connected to the main near the furnace. The common pressures range from 8 to 12 ounces per square inch, but for ores that fuse very readily or when there is no fine ore in the charge to obstruct the passage of the air, 6 ounces may be enough. In some cases a pressure of 16 ounces or more is required. There is considerable

difficulty connected with the determination of the actual quantity of air a copper furnace uses. The volume of air consumed may range from 150 to 200 cubic feet a minute, measured at atmospheric pressure per square foot of horizontal area at the tuyere level.

FIG. 13 FIG. 14

The Green cycloidal blower is somewhat similar to the Connersville blower, but draws the air in at the bottom and discharges at the top, while in Figs. 13 and 14 the air is drawn in and discharged horizontally. Either machine can be arranged in the opposite way, this matter being simply a question of convenience.

43. Blowing Engines.—As the furnaces increase in size the pressure is also increased, so that at present from 6 to 8 ounces is very low. The rotary blower seems to have reached its limitations and has been replaced at one plant by a piston blowing engine patterned after the order of iron-furnace blowing engines.

44. Water Supply.—The quantity of water used in the water-jackets is quite variable. If more fuel is used than necessary, more than the usual amount of water will be needed in the jackets, because the extra heat, not being required for smelting, will more easily warm up the jackets. The amount of water will vary with the judgment of the foreman also. The following is given by one expert as the

maximum quantity of water needed under ordinary conditions for furnaces of different sizes:

TABLE III

Horizontal Area of Furnace at Tuyeres. Square Feet	Water Per Hour. Gallons
3.0	460
5.0	600
7.0	950
9.5	1,100
12.5	1,300
18.0	1,500
24.0	1,800
30.0	2,000
36.0	2,200

It will be noticed that in proportion to its area a large furnace requires less water than a small one. Indeed, a large furnace is generally more economical than a small one in every respect, if there is enough ore to keep the large one running.

45. Vaporizing Water-Jackets.—When a furnace is driven hard, more water is used than is indicated by the above table; but some furnaces probably use less than is shown here. Sometimes, where water is scarce, a small open reservoir is arranged a little higher than the top of the furnace jackets. Water runs from this reservoir by one set of pipes and is delivered to the jackets some distance below their tops; and after being heated, it rises into the reservoir again through another set of pipes connected at the tops of the jackets. Only enough fresh water is supplied to the reservoir to make up for the evaporation and to provide for a little constant

overflow in order to guarantee that the reservoir shall always be full. Although this method keeps the jackets much hotter than the ordinary practice of letting the water run away after once leaving the jackets, the heat cannot burn the jackets so long as they are filled with water. There are chances of sediment forming in the jackets, which will form a crust in time and allow the jackets to be burned, but this happens in either case unless the jackets are cleaned out.

46. Water Reservoirs.—It is considered better practice to draw water from a tank or reservoir some distance above the furnace to insure a constant flow rather than depend on a pump furnishing water direct to the furnace. By whatever means water is delivered to the furnace jackets, it should be at a constant and steady rate, and the overflow from the jackets should be watched to see that there are no stoppages. Of course, it is understood that in case the supply pipe of a jacket becomes clogged there is danger of cracking the jacket, and the attendance, annoyance, and expense connected with replacing it with a new jacket.

BLOWING A FURNACE IN AND OUT

47. The operation of starting a blast furnace is termed **blowing in.** In order to accomplish this operation successfully, the crucible and hearth of the furnace must be thoroughly dried and made hot previous to the introduction of material to be smelted. The bottom tap hole is left open for natural draft and the furnace heated up by charcoal, coke, or cord wood. After a while a light blast of air is introduced at the tap hole by means of a pipe connected with the bustle pipe, in order to increase the heat. This is continued for several hours in order to make sure that the **brasque** in the crucible is thoroughly dry and the whole furnace well warmed. The coke ash is then scraped out through the tap hole and enough fresh coke is charged to come well above the tuyeres, through which air is now blown. When this

body of coke reaches a good, bright heat, small charges of easily fusible slag are shoveled in alternately with fresh coke. When melted slag appears at the tap hole through which draft was at first obtained, this hole is closed. As the crucible fills with melted slag, some ore and flux are substituted for part of the slag charge, and this substitution continues until the regular working charge is being fed. At the same time, the size of the charges is gradually increased so as to fill up the furnace. The force of the blast is also increased until it reaches normal pressure.

48. Slag for Blowing In.—A good slag melts more readily than ore, and when a sufficient body of molten slag has accumulated in the crucible, it forms a reservoir of heat that prevents chilling.

The forehearth is also heated with charcoal or coke and with a light air blast through the tap hole, so that when the slag and matte begin to run into it they will not "freeze."

49. Blowing out a furnace consists in getting out all the molten material in a furnace without chilling it and then stopping the furnace. Naturally, then, the opposite course is taken from that used for blowing in. Slag is gradually substituted for ore, and the rate of feeding is decreased so that the material in the furnace falls to about the level of the tuyeres. With the furnace shown in Fig. 3, the last of the matte and slag are tapped out through the spouts *m*.

CAPACITY OF BLAST FURNACES

50. A furnace such as shown in Fig. 1, with a diameter of 36 inches at the tuyeres, is sometimes spoken of as a 30-ton furnace, which means that it will treat 30 tons of ore and flux in 24 hours. This, however, is hardly correct, because the capacity of any furnace depends on the quality and relative proportions of ore and flux, on the amount

of fuel used, the strength and volume of the blast, etc. In some cases, one of these 36-inch furnaces might not treat more than 20 tons, but with an easily smelting ore it will treat 50 tons in 24 hours if well managed. A rectangular furnace 42 in. × 120 in. at the tuyeres commonly treats from 100 to 200 tons in 24 hours, and in some cases the quantity reaches 250 tons.

PYRITIC SMELTING

51. Objects of Pyritic Smelting.—Iron pyrite, known in chemistry as iron disulphide, FeS_2, loses half its sulphur by volatilization in the upper part of a blast furnace, but the remaining ferrous sulphide, FeS, may be oxidized according to the equation

$$FeS + 3O = FeO + SO_2$$

A good deal of heat is generated by this reaction; and if there is enough pyrite in the charge, the heat produced in this way aids materially in reducing the charge. The term **pyritic smelting** is defined as "a fusion process in which, as far as possible, the sulphureted constituents of the ore are utilized as fuel and also as slag-forming material and as a collector of metals for which the ore is smelted." The process is attractive because it promises to reduce the cost of fuel. But, while a certain amount of heat is often obtained in this way, thus saving part of the coke, and while considerable sulphur is sometimes burned off in a blast furnace without any special attempt to reduce the consumption of coke, certain difficulties have practically prevented the adoption of pyritic smelting. It is found advisable to use from 2 to 5 per cent. of coke to keep the charge from packing so that the passage of air is hindered, especially as pyrite is very much inclined to fall to powder when heated. Even then the sulphur and iron burn so slowly that a furnace treats much less material than when a suitable proportion of the sulphur is removed by roasting previous

to smelting. With low-grade ore, the resulting matte is so poor that it has to go through the process again. In one case three smeltings were required before a matte of satisfactory grade was obtained, and 3 per cent. of coke was used each time. If the ore had first been roasted, the final matte could have been obtained by a single smelting without using any more total coke than in the method that was followed. This would have so increased the capacity of the plant and decreased the amount of handling that in all probability it would have yielded a better profit.

52. Hot Blast.—To increase the oxidation of sulphur and iron, a large amount of air is used with a low pressure and the air is heated before entering the furnace. This use of hot blast causes fusion to begin near the top of the charge instead of confining it to the area just above the tuyeres, as in ordinary smelting. This upper fusion, however, is not thorough, and there is a tendency for half-melted material to stick to the walls of the furnace. When this once begins, it is pretty certain to increase and form obstructions called *scaffolds*, which very much interfere with the operation of the furnace.

53. To illustrate the elimination of sulphur in ordinary smelting, two cases are cited, in each of which practically two-thirds of the total sulphur was burned off by using a large volume of air. The matte resulting contained about 50 per cent. of copper. In the first case the charge contained about 7 per cent. of sulphur and 5 per cent. of copper; in the second case, 8½ per cent. of sulphur and 7 per cent. of copper. If all the sulphur had gone into the matte, extra iron would have gone with it to form ferrous sulphide, FeS, and the matte in the first case would have contained only 33 per cent. of copper and in the second case only 25 per cent. of copper, but there would have been correspondingly larger quantities. This would have made the subsequent treatment more expensive.

54. A blast furnace best adapted to pyritic smelting for copper matte does not differ from the ordinary copper-matting furnace. The process differs, however, in the quantity and character of fuel employed and in the manner of employing it; likewise, the variation in reactions involved by reason of its character. Copper matting is essentially an oxidizing process, and every pound of carbonaceous fuel that it is necessary to use in the process for producing heat is a direct obstacle to the realization of the best results, because in burning such fuel much carbon monoxide is produced, which burns at once in the presence of the necessary heat, thereby robbing the ferrous oxide, FeO, of oxygen and sending the iron into the matte instead of allowing it to combine with silica to form slag. It also robs the sulphur dioxide, SO_2, of oxygen, forming sulphur, and sending that into the matte instead of allowing it to pass into the air as sulphurous-acid gas. Again, it robs the air of oxygen, which is needed to combine with the iron and sulphur of the ore to dispose of them, the one for slag and the other to pass up the chimney and out of the way. There are no reactions involved in copper matting of pyritic ores in which carbon is necessarily desirable, hence it follows that the less of carbonaceous fuel that can be burned in the furnace and the more of the air that can be utilized for heat, the higher will be the grade of matte produced. The utilization of sulphur as fuel involves furnace conditions not vitally necessary to smelting with carbonaceous fuel.

55. This may be better understood by the following example: One equivalent of carbon, C, equals 12, two equivalents of oxygen, O, equal 32; 32 divided by 12 equals 2.667, i. e., the number of pounds of oxygen involved in the oxidation of 1 pound of carbon to carbonic-acid gas, CO_2, produces 14,500 heat units. The sulphur equivalent being 32, when divided by two equivalents of oxygen equals 1; that is, 1 pound of oxygen combines with 1 pound of sulphur to produce sulphur dioxide, SO_2. Then, if 2.667 pounds of oxygen

combining with 1 pound of carbon produces 14,500 B. T. U., 1 pound of oxygen, O, combining with 1 pound of sulphur, S, produces $\frac{14,500}{2.667} = 5,437$ B. T. U. Again, by like comparison, 1 pound ferrous sulphide, FeS, evolves 3,107 B. T. U. in burning to ferrous oxide, FeO. Iron pyrites consist of about 53 per cent. sulphur and 47 per cent. iron. When charged into the furnace, one equivalent of sulphur is expelled at a comparatively low temperature, and hence is not available for heat. The sulphur left then for the production of heat is .265 pound and the iron .47 pound, having a caloric value of 1,460 B. T. U. and for sulphur 1,441 B. T. U., making a total of 2,901 B. T. U. available for heat-producing value of 1 pound of iron pyrites, which is only equal to 20 per cent. of carbon. As the specific heat of air is about 24 pounds, iron pyrites would, in burning, develop sufficient heat to raise the temperature of about 1 pound of air to 12,100°, or 6 pounds of air to 2,070°. As 1 pound of iron sulphide combines in burning with 1 pound of oxygen, and as the air is composed of approximately 4 parts nitrogen to 1 of oxygen, it follows that 5 pounds of air is involved in burning 1 pound of iron sulphide. Assuming the ultimate smelting temperature to be 2,000° above normal temperature, then to raise 5 pounds of air by the combustion of 1 pound of iron sulphide requires the absorption of 1,681 B. T. U., or five-sixths of the heat developed, thus leaving but one-sixth of the developed heat for raising the silica and other constituents of the slag to the necessary fusing temperature. This amount is totally inadequate, *consequently, pyritic smelting with cold blasts is not possible.*

56. Carbonaceous fuel is absolutely necessary where cold air is employed and the method termed pyritic copper smelting then becomes copper matting in the common acceptance of the term. There appears to be no doubt that all copper matting may be efficiently and more economically done by the use of hot-air blasts than without them, and in direct proportion as the air blast is heated the amount of

carbonaceous fuel necessary to be used in the furnace for heat production is reduced.

57. Hot-Blast Advantages.—The evil effect of hot blast in pyritic smelting, which has already been mentioned, is at least partly due to the slow rate of smelting. With the rapid work often done in ordinary smelting, the charge sinks so fast that there is less danger that the zone of fusion will rise. The heat carried in with the air somewhat lessens the amount of coke required in the furnace. There is also another advantage of hot blast over cold blast. The latter somewhat chills the molten material dropping in front of the tuyeres, while the former interferes but very little, and therefore helps to keep the furnace in better condition.

In using hot blast, it is to be remembered that hot air occupies more space than cold air; consequently, to introduce the same weight of air into a furnace, the tuyere pipes must be larger or the pressure greater when using hot than when using cold blast. Air expands .002036 of its volume for each Fahrenheit degree added, and, therefore, if air be heated from 60° F. to 600° F., its volume will increase 2.1 times. This would require that all air pipes and tuyeres be double those necessary for air at 60° F.

58. Hot-Blast Stoves.—There are different methods of heating the blast. Fig. 15 (*a*) and (*b*) shows a pipe stove. Hot gases from a coal fire pass through the space *a* surrounding the pipes *b*, while cold air from the blower enters these pipes at *c* and is discharged hot at *d*. Another method consists in utilizing part of the heat from the molten material in the crucible of the furnace by having an air jacket outside the crucible lining. The heat of the gases escaping from the top of the furnace has also been utilized, both by having air jackets around the hood of the furnace and by placing a system of air pipes in the path of these gases similarly to that shown in Fig. 15 (*a*) and (*b*). It has also been proposed to place air jackets outside of the ordinary

water-jackets, and some even advance the plan shown in Fig. 16.

59. Air-Jacket Theory. To show that this is practicable, assume that an ordinary water-cooled furnace uses 3,000 gallons of water per hour and that this water is heated to 212° F. from 62° F. From 62° to boiling point the water has gained 150° F. of heat. Three thousand gallons of water weigh 25,020 pounds and its heat equivalent is equal to 417 pounds of water per minute raised to a temperature of 150°, or a total of 40,264 heat units has been absorbed; and the temperature of the jackets is now that of water at 212°.

FIG. 15

Assume 150 cubic feet of air per minute or 9,000 cubic feet of air per hour as passing into the furnace. At 62° F., about 13.14 cubic feet of air weigh a pound. Then, 9,000 cubic feet of air will weigh 685 pounds. The specific heat of air is .25, which gives the cooling value of 685 pounds of air equal to 171.25 pounds of water. Then, as 417 pounds of water have been increased

(a)

150° in 1 minute or a total of 40,264 heat units, this latter divided by 171.25, the cooling value of air reduced to terms of water in cooling effect, gives 235° of heat absorbed by the air blast, to which add 62° normal atmosphere, which

FIG. 16

accounts for 297° of heat absorbed by the air blast and jacket. Thus, an ultimate continuous temperature of 297° F. would return to the furnace an equivalent of heat equal to that carried away by 3,000 gallons of water per hour.

60. Furnace Jackets for Heating the Air Blast.—Air is a sluggish conductor of heat, therefore, simply blowing through the jacket to the tuyere would not properly heat

the air or prevent the jacket from melting. To heat the air efficiently and keep these jackets sufficiently cool, the air must be made to strike the heated surface *a* in jets projected through nozzles *b*, as shown in Fig. 16, by means of a pressure behind. This method is said to take up the heat from the iron jackets and transmit it through the tuyeres into the furnace. In case it is thought desirable, that portion of the jacket below the tuyeres may be water-jacketed. While air cooling would be economical and might be feasible, it is questionable whether it will replace water-jackets to any great extent. There can be no doubt, however, of the economy which would result from a highly heated blast derived from the waste heat of the furnace.

SMELTING FOR BLACK COPPER

61. Black copper is the impure metallic product obtained from the blast furnace when treating ores that contain little or no sulphur. It receives its name from the fact that on cooling the surface becomes dull black, due to oxidation. It may contain from 90 to 98 per cent. of copper mixed with from 2 to 10 per cent. of various impurities, such as iron, lead, sulphur, arsenic, bismuth, etc. A few years ago all the copper companies in Arizona produced black copper directly from the carbonate and oxide ores, which were so abundant there. At present, not more than one of those companies, the Copper Queen, does so. Most of the mines have developed such large quantities of sulphide ores that they find it more economical to mix these with the oxidized ores and produce matte, the latter being afterwards converted into black copper. When smelting for black copper in the blast furnace, the slags contain from 1.5 to 2.5 per cent. of copper against .3 to .8 per cent. in smelting for matte.

62. Furnaces for Smelting Black Copper.—The general construction and operation of the furnace need not

differ essentially from that suitable for matte smelting; but the chemical changes that take place are entirely different. In a black-copper furnace, oxygen is taken away from the copper oxide by the carbonaceous fuel and by the carbon monoxide that results from partial combustion of the fuel. On account of the readiness with which black copper chills, a forehearth is never used to separate it from the slag, but the separation takes place in the furnace itself.

63. Black Copper From Roasted Ores.—Black copper can be obtained from thoroughly roasted sulphide ores in just the same way as from the natural oxides or carbonates; but it is more economical to roast such ores only partially, if at all, and make matte, which is afterwards converted into the metallic state. Incidentally it may be mentioned that with a large volume of air under moderate pressure, black copper can be made in a blast furnace even when the charge contains considerable sulphur.

REVERBERATORY-FURNACE SMELTING

64. General Description.—One horizontal and two vertical sections of a reverberatory furnace for smelting copper ores are shown in Fig. 17 (*a*), (*b*), and (*c*). In this process, the ore is fed to the hearth *a* from the hoppers *b* through the openings *c* in the roof *d*. The roof is made in the form of a very flat arch, so as to reflect the heat from the fireplace *e* down upon the hearth. When the charge has fused and the slag separated from the matte, the slag is skimmed out through the door *r*, Fig. 17 (*b*) and the matte is tapped out through the hole *s*. The latter is closed by a clay plug except when matte is being tapped.

65. Construction.—The roof is brought nearer to the hearth as it approaches the flue *f*, in order to compensate for the loss of heat in passing through the furnace. Above

the fireplace *e* there is a passage *g*, which is open to the air at *h*. Air becomes heated in this space and passes through a number of openings *i* into the furnace just above the fire-bridge *k*. This hot air is to assist in burning the gases from the grate fire. The gases from the furnace pass through the sloping flue *f* into the chimney *m*. The flue and chimney must be of ample size to produce a good draft. Otherwise, the furnace will not be hot enough. The flue is 24 inches square at its lower end, and at its upper end, where it joins the chimney, it is 36 inches high by 24 inches wide. The chimney measures 4 feet 10 inches each way inside, which is perhaps somewhat larger than usual for a furnace of this size. It is better, however, to be on the safe side than to have it too small, especially where it is desired to treat a large amount of ore in a given time. The height of the chimney is about 65 feet. On one side of the chimney there is an opening with a sliding iron cover, which should be opened more or less when the doors *o*, *o*, *p*, *r*, Fig. 17 (*a*), are opened. This is done to stop the draft and so prevent cold air rushing into the furnace, which would cool the charge.

66. Hearth Bottoms.—The working bottom of the hearth *v*, Fig. 17 (*c*), is generally made of quartz sand. This sand is put in on top of the brick surface *x* and is thoroughly dried by a moderate fire from the fireplace, the sand being constantly stirred. Any particles of wood, grass, or other organic substance are burned off at the same time. When thoroughly calcined, the sand is worked and pressed into the proper shape for the bottom by means of long paddles. All side doors are then tightly closed and a good, hot fire is maintained for several hours. The sand always contains enough lime, iron, or other base to make the silica fuse slightly under the action of this intense heat. After the fire has been drawn, the furnace is allowed to slowly cool without opening any doors, for fear of producing cracks. Later, a considerable quantity of slag or matte, or both, is introduced and melted down, and is mostly absorbed into the

bottom. This last step is taken in order to prevent the absorption of matte when regular smelting begins. In some cases the working bottom is made of firebrick carefully cemented with fireclay. As these bricks are very dense, they do not absorb nearly as much matte and slag as a sand bottom and require much less repairing, though, of course, they are more expensive.

67. Buckstaves.—The intense heat of the furnace makes the brickwork expand, and on cooling it contracts again. This alternate expansion and contraction would soon destroy the furnace if it were not strongly braced by means of the buckstaves *t* and the tie-rods *u*.

In comparing a reverberatory furnace used for smelting with one used for roasting ores, the chief difference is in the relative sizes of the hearth and the fireplace. A smelting furnace requires much the higher temperature, and therefore has a very much larger fireplace in proportion to the hearth than does a roasting furnace.

OPERATION OF REVERBERATORY FURNACES

68. Matte Smelting in Reverberatory Furnaces. The treatment of ores in reverberatory furnaces is always for the production of matte. Oxidized ores that are to be treated directly for black copper are seldom smelted in reverberatory furnaces, because it can be done more economically in blast furnaces. The changes that take place in the ore are practically the same as in a blast furnace. The ore is stirred, or **rabbled,** considerably through the working doors *o*, *o*, and *p*, Fig. 17, in order to expose all parts of it equally to the heat. This is done with long iron tools shaped like a hoe. When the charge appears to be well fused and the slag separated from the matte, the workmen push their rabbles down through the charge and carefully scrape the hearth, in order to bring to the surface any unfused parts of the charge that may have stuck to the bottom. The furnace is

then closed for some time so as to insure the complete fusion of the charge and allow the matte to thoroughly separate from the slag. The latter is then skimmed off through the door *r* at the front of the furnace, and sometimes also through the doors *o*, *o*. The opening *s* is closed most of the time by a clay plug. When enough matte has collected, a hole is made in this plug by driving through it a pointed steel bar. In general, several charges of ore are fused and the slag from each charge removed before any matte is tapped. The matte is not completely tapped out except when the furnace is to be shut down. By this means there is always a bed of red-hot matte to receive the fresh charge of ore. If the ore were charged directly on the hearth, the latter would be cooled a good deal and parts of the ore would stick to the hearth and remain unfused for a long time. When charged on a bed of liquid matte, the ore spreads out with very little help from the workmen, which is not true when charged directly on the hearth. A furnace of the size shown in Fig. 17 will probably smelt from 30 up to 60 or more tons in 24 hours, depending on the fusibility of the ore, quality of fuel, etc.

69. Slag.—Since any unfused material can be easily removed from a reverberatory furnace and the slag is skimmed or drawn out through the doors instead of having to run out through a comparatively small hole, as in a blast furnace, the same amount of care in regard to the composition of the slag is not as necessary as in the blast furnace. *Fluxes* are not used; and, in fact, the slag sometimes encloses lumps of unfused quartz. However, reverberatory slags do not allow the matte to separate as perfectly as do the blast-furnace slags, and therefore the former carry off more copper. For example, an ore that would yield slag with .5 per cent. copper when smelted in a blast furnace would yield slag with about .7 per cent. copper when fused in a reverberatory furnace.

70. Slag Removal.—Since the slag is removed periodically instead of continuously, as in the blast furnace, it

comes in a very large quantity at one time. On this account it is more difficult to handle. In some cases it is granulated in the manner previously described, but the most common way is to let it run into a series of molds made in a bed of sand on the ground. When cold it is removed to the dump.

71. Fuel.—The expensive fuel, coke, which is used in blast furnaces is not required in reverberatories. Soft, moderately long-flame coal is the common fuel for the latter. Gas-house coke will be found much more efficient for this character of work than coal. More is required per ton of ore, however, than in the blast furnace, because it is not burned in direct contact with the ore. Instead of from 8 to 18 per cent., as in the blast furnace, the quantity ranges from 15 or 20 up to 40 per cent. of the weight of ore. The coal is purposely kept deep on the grate *e*, so that it will not be completely consumed by the air passing through it, but will give off gases to be burned in the hearth *a* and thus generate heat where it is most needed.

72. Producer Gas.—In some works producer gas made from cheap grades of coal is used. In such cases gas and air enter one end of the furnace and the hot waste gases pass out at the other end and through two parallel sets of loosely arranged brickwork, which are made very hot thereby. After a time the valves in the mains are turned to change the direction of the gas and air-currents, so that they pass separately through this heated brickwork and then into the furnace, carrying with them much of the heat which was absorbed by the brickwork. This time the waste gases pass out where the fuel gas and air entered the first time and go through another system of loosely arranged bricks. This alternation in the direction which the gases take continues at regular intervals during the whole process. The loosely arranged brickwork is called a **regenerator,** because it saves or regenerates much of the heat that is usually lost.

COMPARISON OF BLAST-FURNACE AND REVERBERATORY-FURNACE SMELTING

73. Fine ore, that is, ore in which all the particles have a diameter of less than about $\frac{1}{4}$ inch, cannot well be treated alone in a blast furnace. A good deal of the very fine ore would be carried out of the furnace by the blast; and some of it might sift down to and even below the tuyeres without being melted at all. The greatest difficulty, however, is that the fine ore chokes the furnace so that the blast cannot pass upwards regularly. The result of this is that the charge is not evenly heated, and therefore part of it chills and sticks to the sides of the furnace, forming *scaffolds*. When these once begin to form they are almost certain to increase unless the character of the charge is changed, and the furnace will "freeze up" after a while. A certain amount of fine material cannot be avoided, for it is produced by the ordinary handling of ore. In addition to the troubles already mentioned, the capacity of the furnace decreases as the quantity of fines increases.

74. Fine-Ore Treatment.—On account of these difficulties in blast furnaces, fine ore is practically always treated in reverberatories. In cases where the ore is enriched by mechanical concentration previous to smelting, the fine concentrates are usually roasted by themselves and smelted in reverberatories, while the coarse concentrates are treated in blast furnaces. Coarse material can, as a rule, be treated more rapidly in blast furnaces, but in some cases the reverberatory method would be the cheaper. For example, an ore that contained a large percentage of silica would in a blast furnace require much limestone or iron ore for flux; while it might be treated alone in a reverberatory furnace, thus saving the cost of flux. It is to be remembered, however, that the loss of copper in the slag is somewhat greater in a reverberatory than in a blast furnace.

If a smelter receives numerous small lots of ore with varying composition, they can be treated better in a reverberatory than in a blast furnace, because with the latter there

would be much trouble from the necessity of constantly recalculating the amount of flux required. Moreover, with each change in the proportion of ore and flux, the amount of fuel may have to be changed, and by the time the best percentage of fuel has been found by trial a new kind of ore may have to be used.

Most any fuel, however cheap, can be used in a reverberatory; but a blast furnace requires fuel of good quality, coke being generally used, which is expensive.

THE MAHNES PROCESS

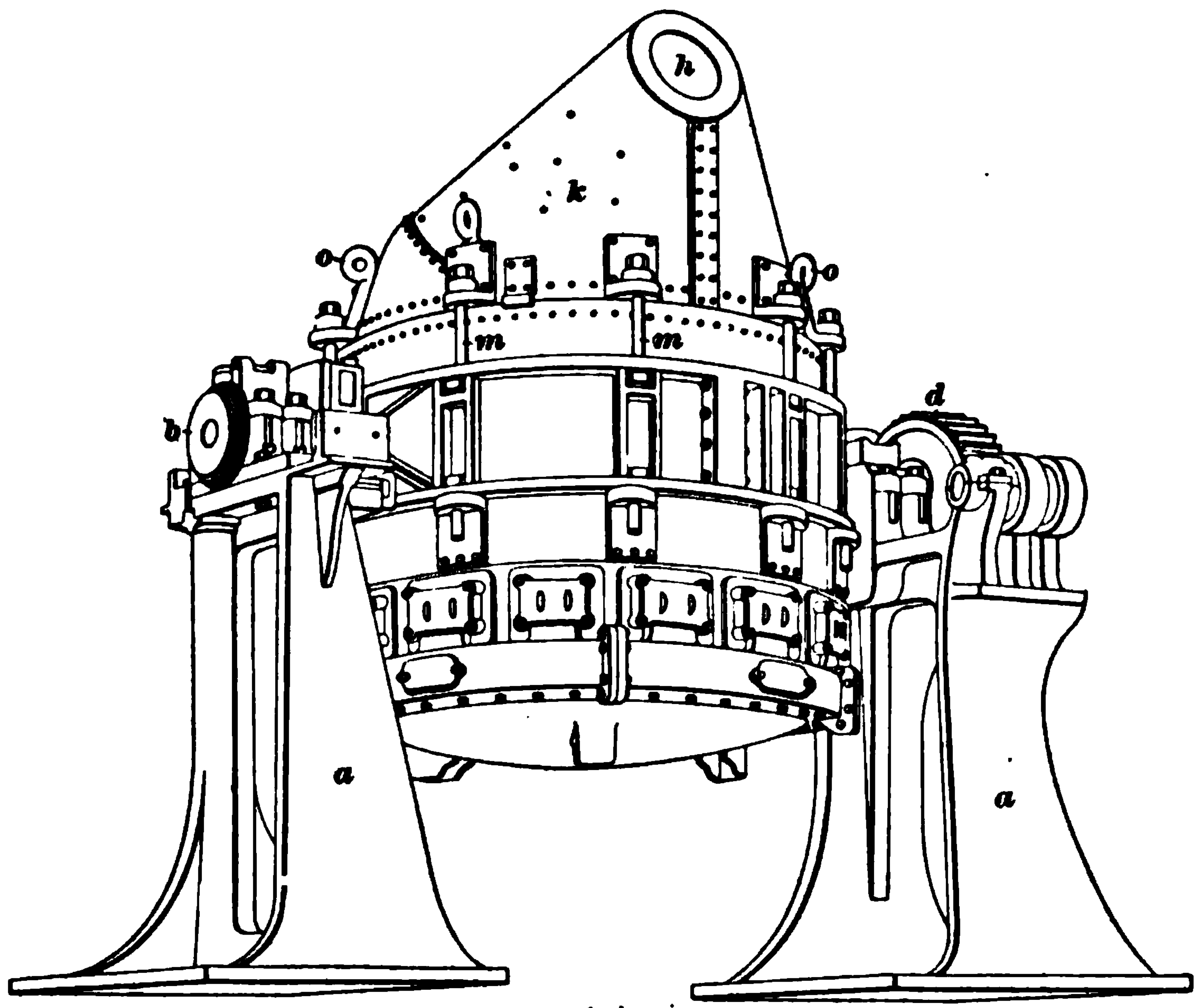
CONVERTER COPPER METHODS

75. The modern method of treating copper matte made in either blast or reverberatory furnaces is called the **Mahnes process,** after the inventor, who lived at Leghorn, Italy. It is also sometimes called **Bessemerizing,** on account of a similarity in mechanical details to the Bessemer process of making steel from pig iron. It consists in oxidizing the sulphur and iron by blowing a strong blast of air through the molten matte. The heat thus generated prevents the large volume of cold air from "freezing" the charge. The sulphur passes off as sulphur dioxide, while the ferrous oxide combines with silica from the furnace lining to form slag.

76. Converters.—The furnace used for this process is called a **converter.** Fig. 18 (*a*), (*b*), and (*c*) show a perspective, a side elevation, and a vertical section of the most common form used in the United States. It consists of an iron shell lined with a mixture of quartz and clay, supported on heavy pedestals *a*, by means of trunnions *b*. It can be revolved on the trunnions by a vertical rack *c* working against the pinion *d* This rack is operated by a hydraulic

piston on the rod *i*, shown in Fig 18 (*b*). The figure shows only the upper end of the cylinder in which this piston works, but this feature is shown in Fig. 20.

77. Blast for Converters.—A blast of air is admitted through one of the trunnions *b*, Fig. 18 (*b*), and the pipe *e*,



(a)

FIG. 18 (*a*)

to the wind box *f*, and from there passes into the converter through a number of tuyeres *g*, shown in Fig. 18 (*c*), which are arranged more than half way round the converter. Sometimes tuyeres are arranged to enter the bottom of the converters.

The blast is supplied by an air compressor, the blowers previously described not being able to produce the required pressure, which ranges from 8 to 20 pounds per square inch.

78. Converter Lining.—To replace the converter lining previously mentioned, the converter is removed from its pedestals and the upper part or hood *k* is lifted off after the bolts and nuts *m*, which fasten it to the lower part, are released. Crushed quartz mechanically mixed with about one-fifth as much clay and a little water to soften the

(c)

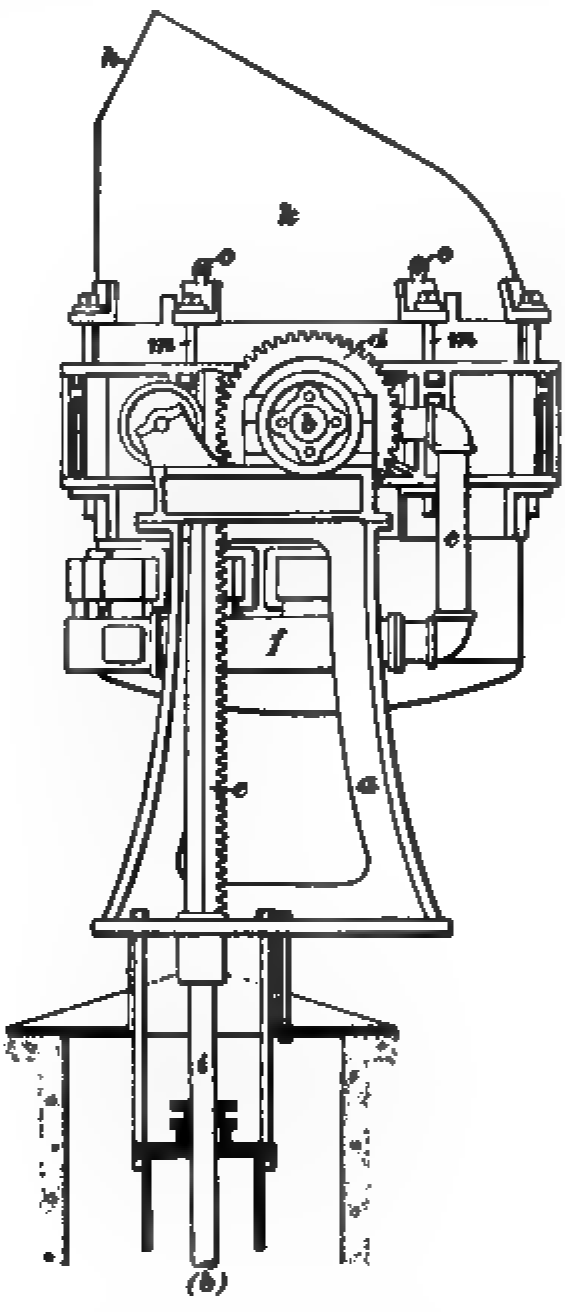


FIG. 18 (*b*) and (*c*)

clay, is then shoveled in. The clay is merely a binder to hold the quartz in place. This is carefully tamped down on the bottom with heated iron pounding bars enlarged at the lower end. When this bottom lining has been made

12 to 18 inches deep, a barrel or core of heavy sheet iron, tapering somewhat towards one end, is put into the converter with the small end down, so that it can be easily pulled out later. There is from 12 to 18 inches space between this core and the converter shell, into which more of the lining mixture is tamped. Tuyere holes are now punched through the lining and the core is removed. The top *k* is fastened in place again and a man gets inside to line this with large lumps of quartz mixture. More clay has to be used here than for the rest of the lining in order to hold the quartz in place. The lining is now thoroughly but slowly dried by means of a light fire made inside of it, after which the converter is replaced on its pedestal. Chilian mills are sometimes used for grinding converter linings, and pug mills for mixing the quartz and clay.

79. Moving Converters.—A common method of moving a converter to and from its pedestal is by a traveling electric crane. The chains of the crane hook into the rings *o*, Fig. 18 (*a*). Sometimes, instead of a crane, a special four-wheeled truck is used. A convenient form of truck has a platform *a*, which can be raised and lowered by a hydraulic piston *b*, shown in Fig. 19. The platform being lowered, the

FIG 19

truck is pushed under the converter; the platform is then raised until the converter is lifted from its bearings, and both truck and converter are moved wherever desired.

80. Charging Converters.—When ready to go into blast, the converter is tipped down, and from 1½ to 5 tons of liquid matte is run into it. When the arrangement of the plant permits, the matte is run directly from the smelting furnace by means of an adjustable, clay-lined iron trough. In other cases, the matte is tapped from the furnace into an immense ladle, in which it is transferred to the converter by a large traveling crane. At one plant the converter is lifted from its supports by a crane, carried to the smelting furnace to be charged directly, and then returned to its place. When the matte has been charged, the converter is brought into the upright position shown in Fig. 18 (*a*) and the blast turned on. The air blowing through the liquid matte oxidizes sulphur and iron. The former passes off as sulphur dioxide into a flue just above the throat *h* of the converter. The iron oxide combines with the silica of the lining to form slag. This makes it necessary to frequently reline the converter. When practically all of the iron has been oxidized, the converter is turned down and the slag is poured off; the converter is then turned up and the blowing continued.

81. Desulphurizing Copper.—Up to this point the copper has not been affected, because it has less affinity for oxygen than have the iron and sulphur. From now on the sulphur is oxidized as before; any copper that becomes momentarily oxidized gives up its oxygen to sulphur. The copper is thus left in the metallic state and settles below the level of the tuyeres. At this stage some of the copper is apt to chill around the tuyeres and close them up. To prevent this, the tuyeres have to be punched with a steel bar inserted from the outside through holes that are tightly covered when not used for punching. After all the sulphur is removed, the converter is turned down and the copper is poured into iron molds. The copper dissolves a certain amount of sulphur dioxide while liquid, which escapes when the metal cools. This escaping gas leaves a blister-like surface, and for this reason the copper at this stage is called

blister copper. It contains about 99 per cent. of copper, together with 1 per cent. of small quantities of sulphur, arsenic, antimony, etc.

82. Reducing Matte to Blister Copper.—A great deal of skill is needed to determine when the iron which the matte contains has all been oxidized and when the sulphur has all been expelled after pouring off the slag. These points are indicated by the varying colors of the smoke and flame that issue from the throat of the converter, by the sound of the blast, and by the appearance of solid particles which are blown out and strike the sides of the flue just above the mouth of the converter. The colors of the flame are white, green, blue, and pink. The white is due to the sulphurous vapors; the other colors to small quantities of vaporized compounds of the different metals. The indications vary more or less with the size of the converter and with the amount and quality of matte put into it for a charge. Hence, a great deal of experience is required to conduct the process. Without proper care, slag may be blown out of the converter and injure the workmen. If the blowing is continued too long, the copper will chill and solidify, and there is likely to be an explosion. The oxidation of the sulphur and iron generates a good deal of heat; but this source of heat, of course, constantly decreases.

83. Relining Converters.—The internal size of a converter increases quite rapidly by the lining wearing away to form slag. The extent of this enlargement is indicated by the fact that a converter which receives 2 tons of matte for the first charge may receive 5 tons for the last charge before being relined. A converter usually treats from 8 or 10 charges before having to be relined. When this becomes necessary, the adhering slag and copper are cleaned out and a new lining is built on to what remains of the old one in the same way as previously described. Usually, when one converter is drying, another is being lined, while the third is in use.

84. Converter Slags.—The converter slag is practically always too rich in copper to be thrown away. From 2 to 2½ per cent. of copper may be considered a fair average of what converter slag will contain, although it is sometimes but little over 1 per cent., while at times it goes as high as 5 per cent. There are different ways of retreating this slag. Sometimes it is poured into a sand bed and when cold broken up and sent to the blast furnace. In one case it is poured into the forehearth of a blast furnace. This should be done, if possible, just after the forehearth has been tapped, so that the converter slag shall not run to waste before the matte it contains has had time to settle in the forehearth. The converter slag may also be poured into a reverberatory furnace a little while before skimming.

85. Leghorn Converter.—Fig. 20 shows a modified form of the Leghorn or trough converter, which takes its name from the city of Leghorn, Italy, where it was first used. Its principal feature consists in having the tuyeres all arranged along one side of the cylinder from *a* to *b*. By this means all the tuyeres are at an equal depth below the surface of the charge, so that, whatever the position of the converter, the air meets the same resistance at all the tuyeres. When the ordinary form of converter, Fig. 18, is in any but a perfectly upright position, the different tuyeres are at different depths below the surface of the charge; and, since the air goes where it meets the least resistance, more will pass through some of the tuyeres than through others.

During the progress of operations, the Leghorn converter can be gradually tilted to keep the tuyeres at a constant depth. As a consequence of this, the required pressure of the air blast is only 5 or 6 pounds to the square inch; while in the ordinary form of converter it is probably never less than 8 or 9 pounds, and in the case of very large converters reaches 18 or 20 pounds. The Leghorn converter is gaining in favor, and it will be seen that instead of resting upon pedestals and trunnions, as does the Anaconda or Parrott

converters, its bearing is a flange which rests upon four heavy rollers *c*. These rollers are grooved at *d* to make the converter run true. The hydraulic jack *e*, which tilts the

FIG. 20

converter, engages with it in such a manner that the rack *i*, in moving up and down as the piston rod of the jack is raised or lowered, meshes with the gear *g* and rotates the

converter. Converters with the piston and rack horizontal are now being constructed. They offer the advantage of having the parts all above ground, where they can be easily reached.

86. Advantages of the Mahnes Process.—The old process of treating the matte obtained from copper ore consisted in a series of roasting and smelting operations. The Mahnes process is much less troublesome and expensive, and it has another important advantage in that it removes the troublesome impurities arsenic and antimony more thoroughly than the old process. In Fig. 21 is shown a

FIG. 21

cross-section of a Leghorn converter in its position to receive the blast. The wind box is at *a*; the tuyeres and

connection with the interior are shown by *b*; the lining for the body of the converter by *c* and for the hood by *d*. The wheels *e* upon which the converter rests and is caused to turn are shown fastened in place by boxes *f* to pedestal *g*, and the latter in turn to bedplate *h*. The dotted lines in the figure show the positions of the converter when filling and pouring.

87. Remelting Matte.—The chief object in matte smelting is to remove the iron by slagging, and the chief object in the blister-copper process is to eliminate the sulphur by combustion. Matte at Butte, Montana, averages 51 per cent. *Cu*, 22 per cent. *Fe*, and 26 per cent. *S*. This proportion is as high as is economical, higher grades requiring more fuel. When the matte is cold enough to handle, it is broken up by sledges to about the size of a man's fist and is fed with limestone and coke into a remelting furnace. The charge is not weighed; the top furnaceman judges from experience the quantities to use, but it is stated that the coke used amounts to 10 per cent. by weight of the matte and the limestone to one-quarter of 1 per cent. of the matte,

Fig. [illegible]

or just sufficient to give fluidity to the skimmings of the well.

In Fig. 22 is shown a remelting furnace for matte, which is seen to be a simple cupola shaft, the main body *a* being supported on four cast-iron pillars, while the lower part *c* is a detachable crucible, shown in section, made of sheet iron, lined with a mixture of 20 parts crushed quartz and 3 parts of the best fireclay. The cupola shaft is also lined with the same material as the well, but decreasing in thickness until it runs out entirely at the feed-door. The crucible is on wheels, in order to reline it more conveniently. The junction *d* between the shaft and the crucible is made by a heavy wall of lining material. This is sometimes broken through by the iron of the melting matte fluxing it out, but when this occurs the lower cupola man patches it with lumps of the lining composition, which he keeps constantly on hand. The tuyeres enter the furnace as shown and have peep holes at *f*. The wind box or bustle pipe *g* connects with the tuyeres by wind pipe *h*. At the rim of the crucible is a cast-iron spout *i* for skimming off slag. The furnace is so arranged that the tap hole *j* is 2 feet above the mouth of the converter. A launder *k* of cast iron, lined with quartz and fireclay, is used to run the matte from the tap hole to the converter.

88. Persistent Elements.—In matte smelting there are two sets of elements, which may be termed the *persistent* and *non-persistent*. The non-persistent are those that may be slagged off almost entirely, such as sulphur, zinc, iron, cobalt, and lead. The persistent elements follow the copper into the metallic state, and are nickel, bismuth, antimony, arsenic, selenium, and tellurium. Dry refining cannot wholly eliminate the persistent elements or separate the precious metals, hence the final copper refining is best accomplished by electrolytic methods, especially where converters are used, and as these are now general, the subject of copper refining will be taken up under electrolysis.

89. Chemistry of the Mahnes Process.—Bessemerizing copper has been touched upon, and only the chemistry of the process remains. Usually there is sulphur enough in the converter to keep up the heat until the operation is completed, but in case the combustion due to sulphur fails to keep up heat, a stick of wood is to be thrown in.

The first action of the air blast going into the converter is to replace the ferrous sulphide and ferrous oxide, converting the sulphur into sulphur dioxide, which will be seen issuing from the mouth of the converter in a dense white cloud. The chemical reaction is according to the equation $2FeS + 3O_2 = 2FeO + 2SO_2$.

The ferrous oxide next comes in contact with the quartz lining and forms with it bisilicate of iron, according to the equation $FeO + SiO_2 = FeSiO_3$. This floats upon the molten copper, the stage being observed by the dense white fumes tinged with rose and green colors that come from the throat of the converter. The rose tint is the first to disappear, followed by the white, while the green becomes more constant. The close of this stage is indicated by a pale-blue color, showing that the iron is entirely combined with the silica. The slag is next poured off and may be used as stated for a blast-furnace flux. When the converter is turned up again and the blast turned on, a scanty blue flame, sometimes mixed with white, appears, which changes to rose, then deepens to red, and finally becomes reddish brown. The change from sulphide to copper is so gradual that the whole charge may be oxidized and become too cool to pour if not closely watched. When the flame shows the operation to be nearly completed, the sparks that are projected against the dust gallery plate are to be watched. If none stick to the plate, the metal can be poured.

90. Cost of Bessemerizing Copper.—At Butte, three converters and one remelting furnace are capable of treating 30 tons of 51-per-cent. matte in 24 hours, at a cost of $6 78 per ton of matte and $13.56 per ton of copper.

One ton of 51-per-cent. matte requires

220 pounds of coke for remelting.
10 pounds of coke for heating converter.
666 pounds silica for lining purposes.
111 pounds fireclay for lining purposes.
5 pounds lime for fluxing.

Cost for labor per ton	$2.93
Cost for silica and fireclay	1.84
Cost for fuel	.98
Cost for blast	.90
Cost for renewals	.13
Cost per ton of matte 51% copper	$6.78
Cost per ton of copper	$13.56

WELSH COPPER SMELTING

91. The Six Steps in the Process.—The Welsh method of copper smelting is carried on in reverberatory furnaces. The different steps in the Welsh process are given, although more modern systems have superseded it, at least, in the United States.

The *first* step taken is to roast the ore in order to expel arsenic and part of the sulphur. This is carried out in a hand-rabbled reverberatory furnace.

The *second* step is for the purpose of dissolving out some of the oxide of iron as a silicate from the roasted ore, and by so doing obtaining a coarse metal.

The *third* step is for the conversion of more of the sulphuret of iron into oxide, and this is accomplished by roasting the coarse metal at a moderate heat for 24 hours.

The *fourth* step in this process is the fusion of the calcined coarse metal to remove all the iron and obtain a fine-metal matte, so termed to distinguish it from coarse-metal matte.

This product contains from 75 to 78 per cent. copper, and is called **white metal** on account of its almost silver color. The slag from this operation is returned to the second operation.

In the *fifth* step or operation, the blocks of white metal are subjected to a combined roasting and smelting process. This is accomplished by gradually heating them with a plentiful supply of air, whereby their surfaces are converted into oxide. This reacts with unchanged sulphide, according to the following equation:

$$2Cu_2O + Cu_2S = 6Cu + SO_2$$

The action continues even after the charge is all melted. The products are blister copper, about 95 per cent. pure, and a rich slag, which is returned to operation *four*.

In the *sixth* step the copper is refined, thereby obtaining commercial copper and a very rich slag, which is returned to operation *four*.

92. "Best Selected" Copper.—Certain impurities, such as arsenic, antimony, and tin, are very difficult to get rid of in the Welsh process as just outlined; and to remedy the difficulty, the process of making what is called **"best selected" copper** was adopted. There are various methods of carrying on this process, but the simplest way is as follows, though with some ores this might not be the best way. The white metal obtained by the fourth operation just described is roasted sufficiently so that, when melted, there is not enough sulphur to combine with all the copper, and part of the latter separates in the metallic state, while the rest remains as matte. A large part of the impurities are absorbed by this metallic copper, so that even after refining it is of low grade; but the copper produced from the remaining matte is of much higher grade than could be produced by the ordinary process.

93. Modifications of the Welsh Process.—The Welsh smelters now receive so much rich material, such as matte, that the first roasting and first smelting operation previously described have become quite unimportant. The rich slags are now treated in small blast furnaces in cases where enough of this slag is produced to keep such a furnace running. The reason for this is that the final waste slag from a blast

furnace carries less copper than that from a reverberatory furnace treating the same material.

At least one of the Welsh smelters has adopted the Mahnes process to convert its *coarse metal* (35 per cent. copper) into *white metal* (75 per cent. copper). The latter, however, is still treated by the old process, because at this particular plant it is believed that the losses are too great when blowing the white metal to blister copper in the converter. It is well known that there is a certain loss in the fumes, especially of silver, if that is present in considerable quantity; but this loss is generally considered to be much more than balanced by the advantages of the converter.

SMELTING NATIVE COPPER

94. As previously stated, the Lake Superior native copper reaches the smelter as a rich product. For smelting purposes it is divided into two grades: the first averaging something over 80 per cent. of copper, the second being considerably poorer because it is still mixed with a good deal of rock. The first grade is simply treated as described under "Fire Refining." The only essential difference in the treatment of the second grade is that a certain amount of lime is mixed with the furnace charge in order to slag the silicious rock.

COPPER REFINING

95. Necessity for Refining.—The metallic product obtained from either of the previously described processes practically always contains at least 1 per cent. and sometimes several per cent. of impurities; and as even a fraction of 1 per cent. of impurity greatly affects the quality of the metal, it must be refined. The chief impurities are antimony, arsenic, and a small amount of sulphur. The two former are the most troublesome and the most difficult to remove. There are two methods of refining: (*a*) fire refining and

(*b*) electrolytic refining. The latter is especially adapted to the treatment of copper containing much silver or gold, because these metals are recovered by this process, but not by the fire process.

FIRE REFINING

96. Refining Furnace.—A refining furnace in horizontal and vertical section is shown in Fig. 23 (*a*) and (*b*). Its general construction is similar to that of the reverberatory smelting furnace already described. The important differences are that in a refining furnace the fireplace *a* is larger in proportion to the hearth *b* than in a smelting furnace; and that the hearth slopes from all directions towards a small well *c* just in front of the door *d*. The blast holes *e* are used in some but not in all furnaces. The sand bottom of the hearth *b* is consolidated by carefully melting into it a quantity of high-grade copper in the same way that slag and matte are used for smelting furnaces. A poor grade of metal used for this purpose would give up some of its impurities to the copper that is refined later.

97. Flapping.—The copper to be refined is introduced through the charging door *f*, the doors are then closed and the charge slowly melted. When the entire charge appears to be fused, a rabble is carefully passed all over the surface of the hearth in order to bring up any unfused metal that sticks there. After fusion is complete and the copper is well liquefied it is **flapped.**

This process consists in agitating the metal by a peculiar motion of the rabble, care being taken to let the latter dip only a little below the surface. The flapping very much assists the oxidation. To produce the proper oxidizing atmosphere, the blast holes *e* are used in some cases to introduce air. In place of this, air sometimes enters through roof passages like *h*, *g*, and *i*, Fig. 17 (*a*), and also through a passage in the fire-bridge *g*, Fig. 23. Not only are the impurities oxidized, but also a considerable quantity of copper. Some of the copper oxide dissolves in the metal and

is very effective in oxidizing the impurities. Some of the impurities, as iron and lead, unite with silica from the sides

(a)

FIG. 33

of the furnace to form slag, which also contains a good deal of copper oxide. The slag is removed several times during

the process, and its copper is recovered either by smelting in a small special blast furnace or by being put in with the regular charge in ore smelting. Sulphur passes off as sulphur dioxide. Some of the arsenic and antimony also pass off as the lower oxides, but a considerable portion of these elements change to the condition of the higher oxides which are not volatile. The latter are to some extent absorbed by the slag, but also partly by the copper.

98. Test Samples.—Test samples of the copper are taken in small ladles as the flapping proceeds. The upper surface of the sample is examined, and the sample when cooled is broken to show its fracture. When the impurities are as thoroughly oxidized as possible and the metal has dissolved considerable copper oxide, the surface of the sample when cold has a slight depression in the middle and the fracture shows a mottled appearance. The copper is then said to be **set.**

99. Poling.—Charcoal is now spread all over the surface of the charge and the end of a long pole of green wood is pushed into it and held down in that position. The heat of the metal causes the escape of steam and other gases from the pole, which thoroughly stir the charge and bring the whole mass into contact with the charcoal. The dissolved copper oxide is reduced to the metallic state by the charcoal and by the reducing gases from the pole. This operation is called **poling.** When it has been carried to just the right point, a sample of the metal has an even instead of a slightly depressed surface after cooling, and the fracture shows a very fine texture and silky luster, while the metal has a beautiful reddish color. The copper is then said to be at **tough pitch** and the refining is complete. The metal is now very tough and can be hammered without cracking on the edges, but the tough-pitch copper still contains a small percentage of copper oxide.

100. Overpoling.—If the poling is continued too long, the copper will be brittle and is said to be **overpoled.** When

in this condition the surface of the test piece will have a slight rise in the center. The accepted explanation is that when the copper is at tough pitch, the very small amounts of arsenic and antimony that still remain and which it is practically impossible to remove are in the comparatively harmless condition of oxide, but that too long action of the charcoal reduces them to the metallic state, in which they are very harmful.

101. Casting Ingots.—When the copper has reached **tough pitch,** the pole is removed, the charcoal is pushed

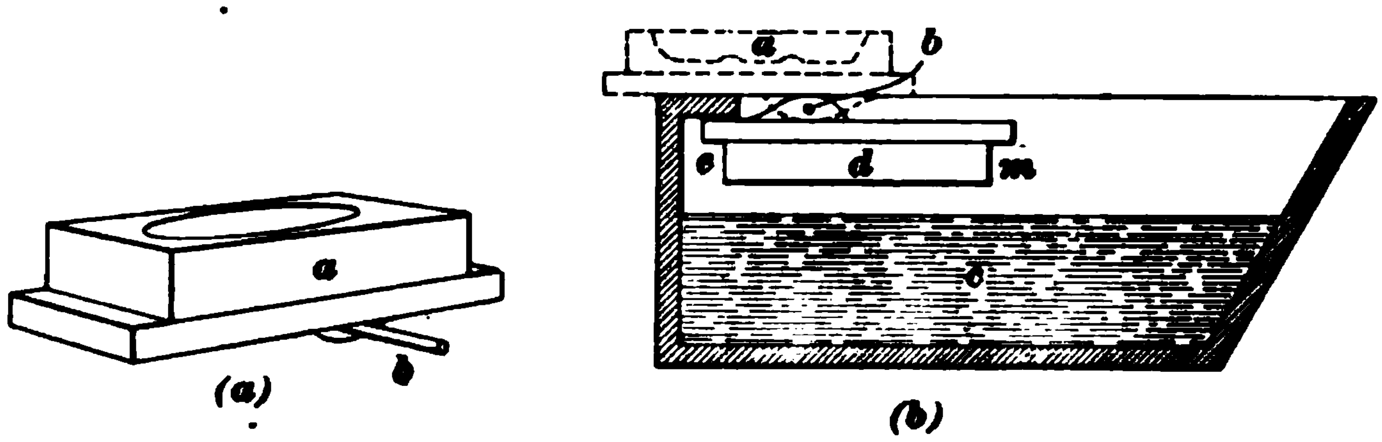


FIG. 24

away from the door *d*, Fig. 23, and the copper is ladled out from the well *c* into molds, forming the metal into what are called **ingots.** The ordinary form of mold is shown in Fig. 24 (*a*). The mold *a* is arranged to swing on the axle *b*, so that when the copper has solidified it can be dumped into the water in the tank *c* by quickly turning the mold into the position *d*, shown in Fig. 24 (*b*). The tank *c* is long enough to accommodate quite a number of molds side by side. The molds are given a wash inside with clay and water before casting commences, to prevent the copper sticking to them. The water, of course, must be dried out before the metal is poured into the mold.

102. Coloring Ingots.—As the copper stands in the molds after being cast, the surface oxidizes slightly; and as this oxidation increases, the color gradually darkens. The ingots are dumped into the water when the color reaches a certain rose-red shade. The reason for being particular in

regard to this shade is that some purchasers imagine this to be an indication of pure copper. In fact, however, this shade can be produced on quite impure copper by certain methods of pickling, though it is more easily produced on pure copper.

103. Mechanical Casting.—The above method of hand ladling is very laborious and therefore expensive. To lessen this item of expense, mechanical methods of casting have been perfected in the last few years. The copper is tapped from the furnace into a large pot or ladle, which can be tilted mechanically. A series of molds, carried on an endless traveling frame, come under this pot in succession and are filled. After the molds have been carried a certain distance and the copper has solidified, the molds are automatically dumped. One of these machines is operated by one or two men, with a helper to apply the clay wash to the molds; while the hand method requires four or five ladlers with one or two helpers. Moreover, because the machine will handle a great deal more metal than can be done by hand, much larger charges can now be treated in a single furnace than formerly. These machines have been adopted at several refineries.

MISCELLANEOUS COPPER-SMELTING MATTERS

104. Flues and Chimneys.—All flues and chimneys should be large enough to produce a good draft, otherwise the furnace work will be greatly hindered. In extensive works there is likely to be a large central chimney, which receives the fumes from all the furnaces. One copper smelter has a circular chimney 365 feet high, with an inside diameter of 16 feet at the bottom and 10 feet at the top. The reason for the taper is that the gases cool as they rise and so contract in volume. This chimney serves for eight roasting furnaces, four reverberatory smelting furnaces, three fair-sized blast furnaces, and two refining furnaces. At another

plant, two flues, each 12 or 15 feet in diameter, extend up a hill to a tall chimney 20 feet in diameter inside. These take the fumes from eight roasting furnaces, five reverberatory smelting furnaces, four blast furnaces. and four converters, all of which are of large size.

105. The tall chimneys just reterred to are considerably higher than necessary to produce the required draft, but they avoid the nuisance of the sulphurous fumes. Except in unusual conditions of the atmosphere these chimneys carry the fumes so high that the wind disperses them before they can settle to the ground.

106. Dust Chambers.—The draft through any smelting furnace is almost sure to carry along a certain quantity of fine particles of the material being treated. When this material is rich enough and is carried away in large enough quantities to pay for catching it, chambers should be provided between the furnace and the chimney, so large that the gases will pass through them very slowly and give the dust a chance to settle. Part of the valuable material carried off by the draft is, however, apt to be in a volatile condition and will only settle when the vapor is condensed.

SAMPLING MATTE AND INGOT COPPER

107. Sampling.—In order to know the quality and value of the various materials and products handled, accurate samples must be obtained. The principles and methods of sampling ores are described in a separate section; but the methods of sampling metallic products and materials that run from furnaces in the molten state are properly described in connection with their production.

108. Sampling Liquid Matte.—A common method of sampling matte or slag is to dip at regular intervals a small ladle into the streams as they flow from the furnace,

from the forehearth, or from the settling pot. The matte is allowed to cool in the ladle, and all the matte buttons obtained in each working shift of 8 or 12 hours are sent to the assayer as one sample. Slag while still liquid is poured from the little ladle into a pail of cold water so as to quickly chill and granulate it. This is done because slag that is quickly chilled dissolves much more readily in acids than if it cools slowly, and therefore is more convenient for the assayer.

109. Sampling Converter Copper.—Copper that is being poured from a converter may be sampled in the same way as matte, or it may be sampled by catching in a pail of water some of the metal that spatters about while pouring into the molds. The test samples taken during the process of refining copper must, of course, be dipped out of the furnace. When pigs of copper are to be sampled after casting, every fifth pig is bored half way through from opposite sides with a steel drill. If there is much silver or gold present, every pig is drilled. Even this method is not likely to give a sufficiently accurate sample if the copper is very rich in silver or gold, because the part of the pig that cools last is generally richer than the part that cools first. This is shown in Fig. 25, where the gold and silver values are indicated for different parts of a pig. The bottom and sides chill first, and the last part to chill is above the center. With large amounts of precious metals the reverse is the case, the richest part being the one to chill first. A method proposed by Mr. Edward Keller consists in casting the copper in large, comparatively thin plates, which are drilled in different places to get a sample. Such plates chill almost as quickly in the middle as at the edges, so that the silver and gold are more uniformly distributed than in a pig. This method is used in at least one place where the copper carries a good deal of silver.

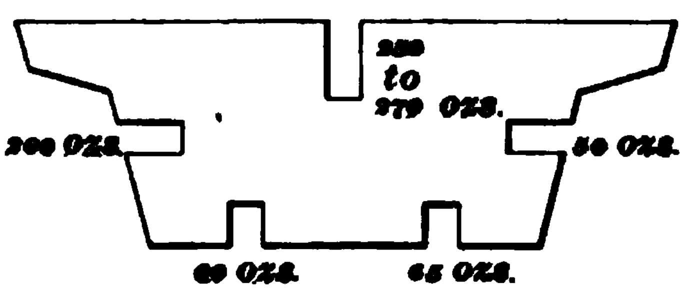


FIG. 25

CHEMISTRY OF COPPER SMELTING

BLAST-FURNACE REACTIONS

110. In the blast furnace, the fuel is burned partly to carbon monoxide CO and partly to carbon dioxide CO_2. The stronger the blast and the more porous the coke, the more the air will penetrate the pores of the coke. The air is thus brought into closer contact with the coke, and this favors the production of CO rather than CO_2. A large proportion of fuel also favors the production of CO. In smelting oxides for the direct production of metallic copper, there should be quite a large proportion of CO, because this is a reducing agent, serving to separate the copper by the reactions

$$CuO + CO = Cu + CO_2$$
$$Cu_2O + CO = 2Cu + CO_2$$

The oxides are also reduced by carbon according to the reactions

$$CuO + C = Cu + CO$$
$$2CuO + C = 2Cu + CO_2$$

111. In smelting for matte, it is desirable to have enough air to oxidize some of the sulphur and thereby produce a richer matte by removing some of the ferrous sulphide FeS from the latter. Under these conditions, there will be but little carbon monoxide CO. The oxidation of sulphur is as follows:

$$FeS + 3O = FeO + SO_2$$

If any copper sulphide is oxidized, the cuprous oxide Cu_2O reacts with FeS, because copper has such a strong affinity for sulphur.

$$Cu_2O + FeS = Cu_2S + FeO$$

112. As previously stated, pyrite FeS_2 loses half of its sulphur in the smelting furnace by volatilization, leaving

ferrous sulphide FeS. In whatever mineral the copper enters the matting furnace, its affinity for sulphur results in its combining to form cuprous sulphide Cu_2S.

113. In the Mahnes converter, after the iron and part of the sulphur in the matte have been oxidized, as shown by the first equation in Art. **111**, some copper is oxidized, and this immediately reacts with some of the remaining copper sulphide to produce metallic copper and sulphur dioxide.

$$Cu_2S + 3O = Cu_2O + SO_2$$
$$2Cu_2O + Cu_2S = 6Cu + SO_2$$

These reactions also come into play in the Welsh process.

114. Any ferric oxide Fe_2O_3 produced by roasting previous to smelting or in any other way is reduced eventually to ferrous oxide FeO. For example:

$$Fe_2O_3 + CO = 2FeO + CO_2$$
$$3Fe_2O_3 + FeS = 7FeO + SO_2$$

The FeO formed may unite with silica in various proportions to form slag; thus,

$$2FeO + SiO_2 = Fe_2SiO_4$$
$$4FeO + 3SiO_2 = Fe_4Si_3O_{10}$$

Other bases, especially lime, form different silicates, and the silicates all combine to make the actual slag. Any Fe_2O_3 that escaped reduction to FeO and entered the slag would make the latter very infusible; but the conditions are practically always such that this trouble does not occur.

115. The reduction of the copper oxide dissolved in the metal during refining takes place by the reaction

$$Cu_2O + C = 2Cu + CO$$

Cupric oxide CuO cannot form in refining, because there is such an excess of copper present that it would be immediately changed to cuprous oxide Cu_2O, thus,

$$CuO + Cu = Cu_2O$$

LEACHING PROCESSES

116. Cement Copper.—Among the many processes that have been invented for leaching copper ores, only a few are in use. Practically all that are now used will be described.

First may be mentioned the fact that in some mines there is a gradual oxidation of sulphides to sulphates. The latter are dissolved by the mine water and the copper may be recovered from this water by passing it through a series of tanks filled with either scrap iron or pig iron. The iron simply replaces the copper, thus:

$$Fe + CuSO_4 = Cu + FeSO_4$$

The finely divided copper so obtained is called **cement copper.** It is always contaminated with considerable iron rust, as well as a certain amount of the scrap iron, and is likely to contain other impurities from the water and the iron.

The production of copper sulphate is much increased when there is a fire in the mine. This has been demonstrated at one of the mines in Butte, Montana, for a number of years.

117. Pyrite Leaching.—Leaching in this manner has been extensively practiced artificially, especially with some of the low-grade Spanish ores at the Rio Tinto mines. Here the ore is made into immense heaps and moistened. Water is periodically passed through the heaps from a system of pipes, and copper is recovered from this water by passing it over pig iron. The following are undoubtedly among the most important chemical changes that occur in the heap:

$$2FeS_2 + 15O + H_2O = Fe_2(SO_4)_3 + H_2SO_4$$
$$Cu_2S + 5O = CuSO_4 + CuO$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O$$
$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S$$

At the Rio Tinto mines the ore has been subjected to this treatment for several years.

118. Heap Roasting for Leaching.—A great deal of Spanish ore has also been roasted in heaps. The chemical changes that take place are much the same as in the slow oxidation process just described, except that a good deal of sulphur dioxide SO_2 is evolved and the process is somewhat shortened. The roasted ore is leached in tanks. Considerable ferric sulphate $Fe_2(SO_4)_3$ goes into solution and this uses up a good deal of iron in the precipitating troughs, according to the equation

$$Fe_2(SO_4)_3 + Fe = 3FeSO_4$$

This loss of iron can be lessened and a certain quantity of copper likewise added to the solution if the ferric sulphate is run through some unroasted ore before being passed over the pig iron. What takes place is shown by the last reaction given in Arts. **117** and **125.**

119. Leaching Chloridized Ores.—Some of the Spanish ore is roasted with salt, producing the following among other reactions:

$$Fe_2(SO_4)_3 + 6NaCl = Fe_2Cl_6 + 3Na_2SO_4$$

The solution of ferric chloride Fe_2Cl_6 obtained by leaching this roasted ore serves to dissolve copper from a fresh batch of raw ore.

$$Cu_2S + Fe_2Cl_6 = 2CuCl + 2FeCl_2 + S$$
$$CuS + Fe_2Cl_6 = CuCl_2 + 2FeCl_2 + S$$

The cuprous chloride $CuCl$ is not soluble in water alone, but is soluble when the water contains considerable sodium chloride $NaCl$ or ferric chloride Fe_2Cl_6; and as there is generally an excess of these, the $CuCl$ is dissolved as well as the cupric chloride $CuCl_2$. Iron is used for precipitation, as in the previous methods.

120. The **Longmaid, or Henderson, process** is considerably used for the treatment of the copper-bearing residues obtained by roasting pyrite for sulphuric-acid

manufacture. If the sulphur remaining in the roasted ore does not exceed 1½ times the amount of copper, some raw pyrite is added, and the whole is ground with 10 to 20 per cent. of common salt. Sometimes the grinding is fine enough for the ore to pass through a screen having 20 holes to the linear inch. This mixture is roasted at a low temperature. A high temperature would cause the loss of copper as chloride, which is quite volatile. Cupric chloride is formed largely by the reaction $CuO + SO_2 + O + 2NaCl = CuCl_2 + Na_2SO_4$, though there is some hydrochloric acid HCl present, which acts as follows:

$$CuO + 2HCl = CuCl_2 + H_2O$$

The HCl forms by the reaction $2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl$. Most of the hydrochloric acid HCl probably escapes from the roasting furnace as a gas, but it is saved by passing the gas through towers in which there is a shower of water. The water absorbs the hydrochloric acid, which is then used to leach the ore after it has previously been leached at least with water. The second water treatment yields a solution containing less copper than the first, and is used for the first treatment of another lot of ore. The solutions are allowed to stand some hours after being drawn off from the ore, in order to settle out the fine ore particles. The copper is then precipitated on scrap or pig iron. During this last step, steam is blown into the tank, partly because the precipitation is done better when warm and partly because the agitation caused by the steam removes the copper from the iron, so that the latter presents a fresh surface constantly.

121. Acid Leaching.—Sulphuric acid is sometimes used to leach low-grade oxide ores or roasted low-grade sulphide ores. The copper is then precipitated on iron, as previously described. Waste hydrochloric acid has also been used. Generally, however, both of these acids are too expensive. Even with cheap acid the process cannot be used for ores that contain much lime or much iron oxide, because both of these consume too much acid.

122. The **Hunt and Douglas process** is interesting as showing the continuous recovery of chemicals to be used again. It is used little and probably not at all for ores, but is used to treat matte containing from 25 to 30 per cent. of copper, 15 per cent. of lead, and about 3 ounces of silver and gold to the ton of matte. The lead would be lost by the Mahnes process. The finely ground matte is roasted to form cupric oxide CuO and ferric oxide Fe_2O_3 and cupric sulphate $CuSO_4$. The roasted mass is then treated in a vat with water containing 10 per cent. of sulphuric acid. When this has taken up all the copper it will, it is drawn off and mixed with a solution of calcium chloride $CaCl_2$ in the proportion necessary to produce the following reaction with half of the copper sulphate $CuSO_4$:

$$CaCl_2 + CuSO_4 = CaSO_4 + CuCl_2$$

The $CaSO_4$ settles out, and into the mixture of cupric chloride and sulphate $CuCl_2$ and $CuSO_4$ is passed sulphur-dioxide gas SO_2 from the roasting furnace, which produces the reaction $CuCl_2 + CuSO_4 + SO_2 + 2H_2O = 2CuCl + 2H_2SO_4$. The cuprous chloride $CuCl$ precipitates, and the sulphuric acid H_2SO_4 is used to leach a fresh quantity of roasted ore. The precipitated $CuCl$ is heated with lime, yielding

$$2CuCl + CaO = Cu_2O + CaCl_2$$

This calcium chloride $CaCl_2$ is used as indicated above and the cuprous oxide Cu_2O is smelted for copper.

The residue left after leaching the copper from the roasted matte is smelted in a lead furnace to recover ,the lead, silver, and gold.

123. Recovery of Silver.—If the ores contain silver, more or less of the latter will be dissolved in some of the processes described above; and if no special attention is given to it, it will be precipitated with the copper. This will sometimes, if not generally, be the cheapest way if the copper is to be refined by electrolysis, because the silver is recovered in that process.

Another method is to precipitate the silver by means of copper before separating out the copper; thus,

$$Ag_2SO_4 + Cu = 2Ag + CuSO_4$$
$$2AgCl + Cu = 2Ag + CuCl_2$$

Still another method, the Claudet process, throws the silver out of solution as iodide.

$$2AgCl + ZnI_2 = 2AgI + ZnCl_2$$

The silver iodide, which separates very readily, is then heated with zinc, whereby a fresh portion of zinc iodide is obtained.

$$2AgI + Zn = 2Ag + ZnI_2$$

The zinc iodide is dissolved in water, leaving the silver behind.

124. Leaching Vats.—All vats and troughs used in the various leaching processes should be thoroughly coated with tar or asphalt. This protects the wood against the rotting action of the various liquors and also prevents the absorption of a large amount of valuable solution.

125. Precipitation by Iron.—The decomposition of the copper solution by iron is effected by the process of replacement; that is, the metallic iron and copper naturally change places, the copper coming out metallic and the iron taking the place of the copper in the solution, thus:

$$\underset{\text{copper sulphate}}{CuSO_4} + \underset{\text{iron}}{Fe} = \underset{\text{iron sulphate}}{FeSO_4} + \underset{\text{copper}}{Cu}$$

This equation shows that 56 pounds of iron can replace or precipitate no more than 63½ pounds of copper, or about $\frac{9}{10}$ pound of iron can replace 1 pound of copper.

The following table shows the results obtained by experiment when using various kinds of iron:

1. Common scrap, such as cans, stovepipe, hoop iron, etc., 8¾ pounds iron for 1 pound copper.

2. Scrap wrought iron, T rail, etc., 6½ pounds iron for 1 pound copper.

3. Scrap cast iron, old grate bars, gearing, furnace doors, etc., 5¾ pounds iron to 1 pound copper.

The grade of the copper obtained using various kinds of iron was as follows:

1. Old cans, hoop iron, wire, blacksmith clippings, etc., precipitate carried 35.5 per cent. copper.

2. Scrap wrought iron, such as T rails, etc., precipitate carried 56.3 per cent. copper.

3. Scrap cast iron, grate bars, furnace doors, etc., precipitate carried 66.4 per cent. copper.

Carefully kept records gave the following as the cost of precipitation per pound of copper produced:

Steam for heating and drying copper precipitate	$.007
Six and one-fourth pounds cast and wrought iron at ½c per pound	.031
Labor-handling precipitates	.002
Sacks, tools, etc.	.001
Total	$.041

The precipitate was handled in a Johnson filter press, dried on a hot plate, and sacked.

LEAD SMELTING AND REFINING

(PART 1)

INTRODUCTION

1. History.—After the metals that occur native, lead is the oldest of which we have historical mention. This is readily explained by its characteristic properties, that is, its ready fusibility and the fact that galena, its principal ore, has a marked metallic luster and is readily reducible to the metal itself. The ancient Egyptians were familiar with lead and used both the metal and its compounds as a glaze for pottery. Its easy fusibility and oxidization render it important in connection with the metallurgy of silver and gold, and these properties were early recognized and commented upon in ancient writings. Similarly, the metal itself has been known in the early history of all the races now recognized as civilized or even semi-civilized, and the lead-smelting industry is very old in both England and Germany.

2. Physical Properties.—Lead has a bluish-gray color, with a brilliant metallic luster on freshly cut surfaces, which soon becomes dull by exposure to the atmosphere. Lead does not readily crystallize; sometimes, however, small octahedra, usually decidedly imperfect, are formed after slow cooling. But as a rule its crystalline nature is only indicated by fern-like appearances on the surface of bars that have been allowed to cool slowly.

It is one of the softest of metals, its hardness in the mineralogical scale being represented by 1.5. It is, therefore, readily cut with a knife or even scratched with the thumb nail. Its softness becomes an indication of its purity, *the purest lead being the softest.* It becomes harder if cooled suddenly or hammered. It is malleable, and when sufficiently pure may be rolled into sheets. It is very deficient in tenacity, so that the smallest lead wire that can be directly drawn is about $\frac{1}{18}$ inch in diameter. Its specific gravity varies slightly with its previous treatment. Cast lead may be said to have a specific gravity of from 11.36 to 11.40, while molten lead has a lower figure—from 10.65 to 10.37, according to the temperature. Impurities usually decrease the specific gravity, but 2 per cent. or less of antimony has the effect of increasing it.

According to the LeChetelier, the fusion point of lead is 325° C., or 617° F. It boils at about 1,500° C., but up to the present time it has not been successfully distilled, although it is rather readily volatilized at high temperatures in contact with air. Its specific heat is low, about .03, also its heat and electrical conductivity. Its property of cohesion is rather remarkable. Freshly cut surfaces can be made to cohere by hand pressure; and when in a state of fine division it may be compressed to such an extent as to form a solid block. Under the combined influences of heating and pressure it may be forced through an aperture and formed into rods and pipes, which is a very important property.

3. Chemical Properties.—When exposed to perfectly dry air, lead undergoes no change; but when the air is moist it becomes covered with a coating of oxide. When exposed to air at the temperature of its melting point or slightly above it, a yellow powder, lead oxide PbO, is formed, which is known as **massicot.** At a higher temperature the oxide formed is of the same composition, but becomes fused and is known as **litharge.** This form is largely obtained in the cupellation of silver-bearing lead. When exposed to the

action of boiling water, no change takes place unless the water has previously been charged with air. The best solvent for lead is nitric acid. Acetic acid also dissolves it, but only when in contact with air. Hydrochloric acid attacks it very slowly on account of the layer of insoluble chloride formed. Sulphuric acid of a density lower than 66°, Beaumé's specific-gravity scale, has little or no effect on lead and is, therefore, concentrated up to this point in leaden vessels. The use of lead in the manufacture and concentration of sulphuric acid forms an important item in its consumption, dependent, of course, on the property just noted.

COMPOUNDS OF LEAD

4. Lead Oxides.—The monoxide PbO is the only one of interest from a metallurgical standpoint. It is yellow in color when formed as a powder, orange when formed in a fused condition; both, however, become buff in color when subjected to grinding, which is the mode of preparing the litharge of commerce. Litharge is readily fusible, the temperature being given as 954° C., and it is volatile at high temperatures. If cooled quickly from a molten condition, it is yellow in color; slow cooling produces a somewhat reddish tint. It is very slightly soluble in water. Other forms occur, but they are of no especial interest to the metallurgist. *Molten litharge unites with silica and acid silicates and, therefore, corrodes acid-refractory materials. It forms fusible compounds with many of the oxides that may in themselves be quite infusible.* This fact is of the highest importance in certain metallurgical operations, a particularly comprehensive illustration of its application being found in the cupellation and scorification of lead buttons in assaying for gold and silver. In combination with lime, baryta, magnesia, etc., litharge plays the part of an acid. It is very readily reducible by hydrogen, carbon, and carbon monoxide; and on being mixed with many substances, such as copper, zinc, iron, tin, antimony, bismuth, and arsenic,

it is reduced to a metallic condition, while a corresponding amount of the metal thus treated is oxidized. These oxides fused with the litharge are readily volatilized, scorified, or dissolved by the cupel material.

Red lead Pb_3O_4 is used rather widely in the arts, and it may be of interest to know that it is made by oxidizing metallic lead to PbO at a temperature somewhat below the fusing point of litharge, and then further oxidizing the resulting powder at a still lower temperature.

5. Lead Silicate.—Lead oxide and silica combine in almost all proportions. The fusibility of such compounds decreases with an increase in the proportionate amount of silica. The combination is best effected at the temperature at which the oxide is merely softened; if it is entirely fused the reaction is impeded. All silicates containing less silica than that expressed by the formula $2PbO.3SiO_2$ are readily fusible to a transparent glass, the singulosilicate $2PbO.SiO_2$ forming a very mobile liquid. As the proportion of silica is increased, both fusibility and fluidity after fusion decrease until finally the materials merely frit together, probably the result of a cementing of particles of silica by lower silicates.

The glasses formed by the silicates high in lead oxide are readily colored by other metallic oxides and give rise to the colors noted in scorification cups in assaying; for example, iron gives a brownish color; copper a green; cobalt a blue; chromium a red; manganese a chocolate brown; and lead a yellow-lemon color.

Lead silicate once formed is difficult to reduce to metallic lead; and to effect its complete recovery, the silica must be set free by the addition of some stronger base, such as metallic iron.

6. Lead Sulphide PbS. — Lead sulphide, known as *galena*, forms the principal ore of lead and when pure contains 86.6 per cent. of the metal. It is formed artificially by heating lead and sulphur together, by the reduction of lead sulphate with carbon, and by precipitation from a solution

of lead salts with hydrogen sulphide H_2S. In whatever way it is prepared its properties and qualities are the same. It fuses at 935° C., that is, at about the same temperature as litharge. The resulting liquid is very thin and easily penetrates the small fissures or cracks in brickwork. Away from contact with the air it is rather readily volatile, beginning at temperatures slightly lower even than its melting point. From such volatilization crystals of artificial galena result, having the typical cubic form of the mineral. These are frequently found in the throat of the lead blast furnace. Molten galena mixes with lead in all proportions. This has given rise to the theory that subsulphides of lead exist; it has been quite conclusively proved, however, that these are nothing more than mechanical mixtures, as on standing the mass separates more or less completely into metallic lead and the monosulphide. In the blast furnace practically no sulphur is found in the clean base bullion, and any lead that may remain in combination with sulphur is found with the matte, since ample time for separation is afforded. This separation is further facilitated by the fact that PbS is amorphous with cuprous sulphide Cu_2S and ferrous sulphide FeS.

7. Reduction of Lead Sulphide.—Lead sulphide heated in contact with air, especially in a state of fine division, forms lead oxide or lead sulphate. This, of course, is the action taking place in the ordinary roasting furnace. The complete reduction of lead sulphide is best effected by metallic iron. Metallic copper alloys with the lead formed, while the cuprous sulphide Cu_2S retains some PbS. Zinc sulphide is so infusible that it forms a sintered mass with the lead and lead sulphide, which is incapable of further chemical action. The simplest form of the reaction between lead sulphide and metallic iron may be expressed as follows:

$$PbS + Fe = FeS + Pb$$

Probably in practice some PbS is retained with the FeS, but since there is a certain elimination of sulphur dioxide SO_2 in furnace work, the above reaction is used as the

basis of calculation in making up charges. Basic silicates of iron also give their excess of iron to reduce lead from its sulphide in the blast furnace.

8. Air as a Reducing Agent.—To some extent, not fully determined, calcium monoxide CaO and barium monoxide BaO act as reducers of lead from its sulphide. With access of air the reaction may be expressed as follows:

$$4PbS + 4CaO = 3CaS + CaSO_4 + 4Pb$$

Away from air, in the presence of carbon, the probable form is

$$2PbS + CaO + C = Pb + (PbS.CaS) + CO$$

9. Lead-Sulphide Reactions. — Since lead sulphide forms the principal ore, it is well to mention here with special emphasis the reactions that take place between it, lead oxide, and lead sulphate. The practical application will be discussed later. At a bright-red heat the following reactions will take place:

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$

If the $PbSO_4$ be in excess, only oxide will be formed, with elimination of SO_2, as expressed by

$$PbS + 3PbSO_4 = 4PbO + 4SO_2$$

10. Lead sulphate $PbSO_4$ occurs in nature as the mineral **anglesite.** It is also formed in a metallurgical way by roasting lead sulphide PbS. It is one of the most stable of the metallic sulphides and the complete removal of sulphur by the usual method RSO_4 heated $= RO + SO_3$ is extremely difficult. Even at a white heat sulphur trioxide SO_3 is only removed in part, the lead remaining as a basic sulphate. It is very refractory and only softens at a high temperature. Basic sulphate would be reduced by the carbon of the blast furnace to lead sulphide; when, therefore, it is thought necessary to remove the sulphur entirely, the SO_4 radical must be replaced by silica SiO_2, which at a high

temperature is the stronger radical. This forms lead silicate and SO_2 or $SO_2 + O$ are set free. This subject will be discussed under the heading "Slag Roasting." It should be noted, however, that some sulphur is always removed in the blast furnace as sulphur dioxide SO_2, by the reaction between $PbSO_4$ and PbS, as given above, so that the complete removal of sulphur is not essential in practice.

11. Lead carbonate, which occurs in nature as the mineral **cerusite,** is not of importance in metallurgy, for at a temperature below a melting point of lead it is broken up into lead oxide PbO and carbon dioxide CO_2.

12. White lead is a basic carbonate, probably $Pb(OH)_2.2PbCO_3$, whose manufacture enters largely into the field of the metallurgist.

LEAD ORES

13. Lead Deposits.—Lead is not often distributed in such quantities as to form deposits sufficiently rich to be classed as ores. Only three minerals are of sufficient importance to come under such a classification, namely, *galena*, *anglesite*, and *cerusite*.

Galena is sometimes found in comparative freedom from other materials, but it is frequently mixed with non-metallic vein matter or with that and other metallic sulphides. The possibility of its concentration depends largely on the nature of this occurrence. In the United States the only ores concentrated to any extent are those of southeastern Missouri, where coarsely crystalline galena is found in a gangue of dolomite. The ore as taken from the mine contains about 6 per cent. of lead and is remarkably free from other sulphides. In all other localities of commercial importance in this country, in order to be classed as an ore, the mineral as taken from the mine must be sufficiently rich in lead to be smelted, either alone or in a mixture with other minerals, without concentration.

14. Gold-Silver Lead Ores.—A very notable fact is that silver and gold are almost invariably associated with galena. The amount of silver varies very widely. The gold is almost always small in amount, but is equally certain to be present. In the galena itself the silver is probably present as isomorphous silver sulphide, replacing the lead sulphide. It may be, and frequently is, present in associated minerals, but this is accidental, whereas the other is invariable. The form in which the silver is present must be taken into account in any concentrating operation, since, if merely associated, it is much more readily lost in slimes.

15. Oxidized Lead Ores.—*Cerusite* and *anglesite* are classed together as **oxidized ores.** Both are the result of the decomposition of galena; anglesite is formed first, and is afterwards, by contact with earthy carbonates, changed more or less completely into cerusite. These minerals are much more uncertain as to their silver contents than is galena. The silver present is mainly in the form of chloride with possibly some sulphide and antimonide; therefore, its solubility is quite different from that of galena, so that leaching causes much irregularity. The ores are classed as *hard*, and *soft* or *sandy*; they are very irregular in lead contents, because the agencies that cause the oxidization of the galena may have introduced much oxidized or altered vein matter. On account of this and the probable fine state of division of the lead compounds, these ores are much more difficult to concentrate. The losses are high, especially in silver, and concentration is therefore less frequently attempted even than in the case of galena.

16. Location of Lead Ores.—In the United States, the non-argentiferous ores of lead occur principally in southeastern Missouri. The Joplin district, in which galena is associated with zinc blende is not producing much at present. The silver-bearing ores of lead, both oxides and sulphides, are found in the Rocky Mountain district and on the Pacific Coast. In these the lead ore is associated to a greater or less extent with other metallic sulphides and impurities.

The fact that the ores have been concentrated to a high-grade product and are very low in silver contents gives rise to methods of smelting in the Mississippi Valley district that are entirely different from the methods used in the West for the impure silver-bearing ores.

ALLOYS OF LEAD

17. The **alloys of lead** with silver and gold are of special importance, as they form the bases for the recovery of a large proportion of these metals. Other metals form alloys of commercial importance, while still others are deleterious and may be regarded as impurities.

18. Lead-Silver Alloys.—Silver alloys with lead in all proportions, though there is a definite proportion, namely, about 650 ounces per ton, which is pointed to by some of its physical properties as an **eutectic**; that is, when it melts at a low temperature. Up to this proportion silver lowers the melting point of the alloy; beyond it, the melting point rises. The amount of silver left in lead after desilverization by modern processes is so small as to be negligible in its effect on the lead for mechanical and chemical purposes.

19. Lead-Gold Alloys.—Gold alloys with lead in all proportions, but it is not usually present in sufficient quantities to have any noticeable effect on the metal.

20. Lead-Copper Alloys.—Copper may be mixed with lead if both are heated above the melting point of copper, but it separates again on cooling unless the mixture is chilled quickly. A minimum of .08 per cent. of copper remains in the lead, which, however, is practically removed in the Parkes process of desilverization. The separation of copper from the base bullion in the crucible of the blast furnace causes the mass to assume a mushy condition and leads to trouble in tapping. Small amounts of copper in commercial lead have no effect, as far as mechanical treatment is concerned or on its use in the manufacture of white lead.

The limit for the latter ranges from .0014 to .003 per cent., while copper in commercial lead desilverized by the Parkes process, which is described in *Lead Smelting and Refining*, Part 2, never appears beyond the fourth decimal place. In such small quantities copper has little or no effect on the lead when used in the sulphuric-acid industry; in the manufacture of glass it is decidedly objectionable.

21. Lead-Bismuth Alloys.—Bismuth alloys with lead in all proportions, small amounts having no effect upon its chemical or mechanical properties. Bismuth is not materially removed by the Parkes process, but is largely reduced by the Pattinson process, described in *Lead Smelting and Refining*, Part 2. In lead desilverized by the former method it may appear in the third decimal place; by the latter method it is usually only in the fourth decimal place.

22. Lead-Tin Alloys.—Tin alloys with lead in all proportions, but it is not often found in market lead. It forms a useful alloy in the manufacture of solder. Its effect on lead is to increase its hardness and decrease its fusibility.

23. Lead-Antimony Alloys.—Antimony also alloys with lead in all proportions, but it makes the lead hard and less malleable. It is rather common as an associated mineral with lead ores and usually must be removed before the subsequent treatment of base bullion for the recovery of the precious metals. For white-lead purposes antimony should not run higher than .05 per cent. It is removed by subjecting the lead to oxidation in a reverberatory furnace, where it is concentrated in the skimmings from this furnace, then resmelted in a separate blast furnace to hard lead and sold as such. Hard lead is used as a basis for antifriction alloys, type metal, etc. In market lead desilverized by the Parkes process, antimony does not appear above the third decimal place.

24. Lead and Iron Alloys.—Iron does not alloy with lead to form a metal of importance. The maximum amount found in lead is .07 per cent.

25. Lead and Zinc Mixtures.—Zinc can be mixed with lead in varying proportions, but separates to a large extent upon cooling. The amount that will remain permanently alloyed is dependent on the temperature of the lead. Lead at 400° C. retains .6 to .8 per cent. zinc; lead at 500° C. retains .9 to 1.3 per cent. zinc; lead at 600° C. retains 1.5 to 2.3 per cent. zinc; lead at 700° C. retains 3.0 per cent. zinc. It is removed by oxidation in the reverberatory furnace or by agitation in a kettle with steam. It injures lead for both mechanical and chemical purposes, making it hard and brittle and readily attacked by acids.

MERCHANTABLE LEAD

26. Commercial Alloys.—The chief commercial alloys are type metal, a compound of lead, tin, and antimony in various proportions; and journal-bearing metal, of the same components, but in different proportions. Shot contains a very little arsenic, less than one-half of 1 per cent. Solder is a mixture of lead and tin.

27. Production.—The lead production of the United States in 1899 was as follows: Desilverized, 171,000 short tons*; soft, from non-argentiferous ores, 40,000 tons; antimonial, 7,000 tons; total, 218,000 short tons.

In 1898 the United States produced 207,000 metric tons as against 193,000 by Spain, 132,000 by Germany, and 71,000 by Mexico, out of a total world's production of 782,000 metric tons.

28. Uses.—The approximate distribution of lead among various manufactures in the United States is as follows: Pigments, 35 per cent.; lead pipe, 20 per cent.; shot and bullets, 9 per cent.; sheet lead, 8 per cent.; miscellaneous, 28 per cent.

The market lead, as purified by modern processes, contains so small an amount of impurities as to render them almost negligible. It should not run less than 99.98 per cent. lead and often runs 99.99 per cent.

* Short ton = 2,000 pounds; metric ton = 2,204.6 pounds; long ton = 2,240 pounds.

METHODS OF LEAD EXTRACTION

29. Lead Reduction.—It has been found impracticable to obtain lead from its ores on a commercial scale in any wet way, consequently it must be treated by igneous methods. Here, as in copper smelting, two alternatives are presented. On the one hand the lead can be reduced to a metallic state and fused while the foreign materials remain more or less unaffected by heat; the lead will then flow out from the mass and can be separated from it. From these conditions it will be readily inferred that only a high-grade material can be treated by this method. On the other hand the whole mass may be fused while the lead alone is brought to a metallic state; then, by difference in specific gravity, the reduced metal separates from any metals that may be present in combination with sulphur, and these, in turn, separate from metallic or earthy silicates. The choice of method and the means of bringing about the desired result are dependent, of course, on the chemical properties of the various constituents of the material to be treated and it is for this reason that the nature of lead and its compounds has been treated so fully.

30. Reverberatory Smelting Conditions.—In reviewing what has been said, it will be found that galena, the principal source of supply, is fusible, volatile, and when in a state of fine division and exposed at a moderate temperature to the atmosphere, rather readily converted into lead oxide and lead sulphate. Looking farther, it will be noticed that lead sulphide plus lead oxide or lead sulphate gives off at a moderate temperature sulphurous anhydride and leaves metallic lead. This furnishes a method for the reduction of the lead to a metallic state at a temperature sufficiently low to avoid the fusion of accompanying materials. It can be conveniently accomplished in the reverberatory furnace, where constant manipulation is possible, and forms the basis of what is known as the reverberatory method of lead smelting. This method, however, is limited to ores that contain

at least 60 per cent. of lead, and therefore it is not available for most of the lead ores mined in the United States, especially those carrying either gold or silver or which are associated with gold and silver minerals. It also effectually precludes a mixture of **dry ores** containing gold and silver, but no lead, with ores containing lead. One of the most valuable purposes for which lead serves is as a collecting agent for the precious metals.

31. Blast-Furnace Smelting Conditions.—Turning again to the properties of lead compounds, it is found that lead oxide is reduced by carbon monoxide to metallic lead; also that lead is reduced from its silicates by stronger bases. If the ore is previously roasted so as to change the lead sulphide into lead oxide and thus eliminate the sulphur, then sufficient material, known as flux, added to form a fusible compound called **slag,** when combined with all materials other than lead in the roasted ore, and the whole charged into a blast furnace with alternate layers of fuel in proper amount, the following reactions will take place:

1. The carbon of the fuel and carbon monoxide produced from it will reduce lead oxide to metallic lead.

2. The bases essential to the slag will liberate metallic lead from any silicates that it may have formed.

3. Sufficient heat will be generated to fuse the entire mass.

The molten products may then be allowed to separate by gravity, and under proper conditions it will be found that the precious metals have been very effectively collected from their ores by the lead. This method is known as *blast-furnace smelting*, and while it also has its limitations, they are much broader than those of reverberatory smelting. It is, therefore, the method most generally used in the United States.

32. Hearth-Smelting Conditions.—A third possible method of lead extraction consists in an intermediate course,

known as *hearth smelting*. In this, however, the limitations are even narrower than in reverberatory smelting, and it is of correspondingly smaller utility. In some exceptional cases, however, it has its advantages and will, therefore, be fully described.

REVERBERATORY SMELTING

33. The following reactions occur in roasting galena:

For slow roasting,

$$2PbS + 7O = PbO + PbSO_4 + SO_2$$

For quick roasting,

$$3PbS + 10O = 2\,PbO + PbSO_4 + 2SO_2$$

34. Reverberatory-Furnace Construction.—Where reverberatory lead smelting is practiced in the United

Fig. 1 (*a*)

States, the type of furnace used is shown in perspective in Fig. 1. Such furnaces will probably average 12.5 feet by

20 feet outside diameter, with a hearth or inside measurement of 10 feet by 13.5 feet. The furnaces are constructed of red brick outside, but are lined with firebrick of special refractoriness inside. Fig. 1 (*a*) shows the side of the furnace, reproduced from a photograph, thus showing the every-day working appearance with tools lying around. *c* is the furnace door, *d* the working doors, *e* the tap hole, *k* the kettle under the tap hole to receive the lead. This

FIG. 1 (*b*)

furnace was covered with cast-iron plates on this side, which were held in place by buckstaves, plates *a*, and rods *b*. The pig lead is seen stacked up at the left. Fig. 1 (*b*) shows the other side of the furnace with the working doors *d*, a tapping hole *e*, and receiving kettle *k*. The ore is charged into the furnace from hopper *f*. The rabble, or hoe, *g* with which the ore is worked is shown on the floor.

35. Plan of Reverberatory Furnace.—The plan of a reverberatory smelting furnace is shown in Fig. 2. In the figure *a* is the hearth, *b* the grate bars of the furnace, *c* the

(a)

FIG. 2

bridge over which the flames pass into the furnace, *d* the flue through which the gases escape from the furnace to the chimney *s*.

Fig. 2 (*b*) shows a longitudinal section of the furnace on the line *x y*. The working bottom *a*, which is constructed on the firebrick hearth, is made up of old slag coarsely broken and mixed with a small amount of sand. This material is added in successive layers, each layer being heated until soft and then rammed into shape by means of iron tools. Another layer is then added and so on until the floor assumes the appearance shown in the figure. The tap hole is under the second door from the bridge wall; consequently the floor is given a slight inclination to that point. In the figure, *b* shows the firebox, *c* the bridge wall, *d* the flue to the stack *s*, and *f* the feed hopper above the furnace.

36. Smelting Ore.—The ore used for reverberatory smelting is pure galena occurring in a dolomite gangue. It is concentrated so that it runs about 70 per cent. in lead. In the process of concentration it is sufficiently reduced in size to be well adapted for reverberatory smelting. The charge consists of about 3,500 pounds and is placed in the conical hopper *f* at the top of the furnace. After the slag of the previous charge has been fully removed, the ore is dropped upon the hearth, which is still moderably hot and spread out by means of the rakes *g*, shown in Fig. 1 (*b*). The fire is kept low and open and air is freely admitted both through the firebox *h* and the working doors *e*, which are open more or less to permit the turning and mixing of the ore upon the hearth with the iron paddles, shown in Fig. 1 (*a*).

The temperature is not allowed to rise to a point at which the furnace charge will be fused to any extent. For a charge of the size mentioned, this operation should continue about 5 hours. At the end of that time fresh fuel is added to the firebox and all surplus air is cut off. The temperature is then gradually raised and lead flows freely towards the lower part of the hearth. As the lead ceases to flow the temperature is raised more and more and the residue upon the hearth worked, by means of the rakes, in order to free any lead that may be mechanically retained. This stage

lasts about 7 hours, and the smelting is carried no farther. At the conclusion of the operation, the lead is tapped, and the slag, which is at a bright-red heat and about the consistency of thin mud, is raked out of the working doors. The lead resulting from the treatment of a single charge amounts to about 2,000 pounds.

The slag contains from 35 to 40 per cent. of lead, and no attempt is made to extract the **slag lead** in the reverberatory furnace. In this way the lead obtained is pure and of high grade and commands a ready market. The slag is sold to smelters using the blast-furnace process; this is the weakest point in the reverberatory process, for it renders the smelter dependent on others for a slag market.

37. English Practice.—This is probably the most economical process for the extraction of lead in the reverberatory furnace; it competes very successfully with other processes and on equal terms with them. The process is decidedly modified in some of the foreign smelting works.

In English practice each part is treated by several distinct and successive oxidations and reductions, the first oxidation being purposely incomplete. In some localities the entire charge is melted down into the lead well one or more times; then 1 or 2 per cent. of slaked lime is thoroughly mixed in to stiffen the slag, and it is again "set up" on the hearth for further oxidation and reduction. It is aimed to extract all the lead in the reverberatory furnace; that is, the slag is treated for the extraction of the slag lead in the same furnace and the whole process is pushed much more rapidly than in the United States. The arrangement of the hearth and lead well are practically the same as in this country.

38. Silesian Practice.—In the Silesian method of lead smelting, a large furnace with the lead well in one corner at the flue end is used. The requirements for this process are slow roasting, the avoidance of fusion, and the use of several stages. After each successive oxidation and reduction, however, fresh material in the form of by-products from other operations is added to the charge. It is not

attempted to extract all the lead in the reverberatory furnace; its slag is resmelted in the shaft furnace.

39. Recapitulation.—A comparison of results shows that slow roasting without forcing the operation yields more lead, with a proportionately smaller consumption of fuel. An authority on the subject has said: "Rich, pure, non-quartzose ores should always be treated by this latter method. The operation should take place in large reverberatory furnaces with easy access of air and provided with a single fireplace and a receiving basin, internal or external, placed in the least heated region of the furnace. The operation should always be conducted slowly, and should consist of two very distinct phases, *roasting* and *reaction*, i. e., mutually reducing action. For roasting, the layer of ore must never exceed 3.5 inches in thickness.

"Roasting is to be effected at a low temperature, and should proceed as far as the theoretical limit of one equivalent of sulphate or two equivalents of oxide for each equivalent of sulphide. After the first firing, which produces lead, and fresh roastings and firings are twice or thrice repeated, the rich residues, called **gray slags,** must be withdrawn from the reverberatory furnace, without having recourse to **ressuage,** i. e., reduction of those residues in the same furnace immediately afterwards, as in the Cornish and Bleiberg processes, but rather by practicing this ressuage in a blast furnace."

40. American Practice.—It will be seen that the American process conforms to this statement in every respect, except that of repeating the roasting and reduction; and under the conditions prevailing in this instance, it is probably no loss to send the slags after one treatment direct to the blast furnace.

For districts where a small amount of high-grade ore is produced, the reverberatory method has the advantage that the roasting and reaction take place in the same furnace and that it is a comparatively inexpensive one. No variety of ores is required to make up suitable charges, and fluxing

of the small amount of gangue is unnecessary. If supplemented by the blast furnace, the ultimate recovery of both lead and silver is sufficiently good ; and on account of the low temperature, as noted, losses by volatilization are comparatively small. On the other hand, the amount of fuel and labor required is high and the labor must be skilled. In some localities the process has been given up on account of the difficulty in obtaining properly skilled labor.

41. The Reverberatory Smelting Process.—The ore, which may consist either of galena or of a mixture of galena with a small amount of oxidized ore, is first crushed so that it will pass through a screen with about 5 meshes to the linear inch, in order that the roasting may take place to advantage. It is then charged into a reverberatory furnace that is already heated to a moderate temperature by the previous operation. The hearth of the furnace is so constructed as to slope from all directions towards one point, which is depressed and serves as a well for the collection of the metallic lead when formed. The ore is spread out in a comparatively thin layer, care being taken to keep it out of the well; air is supplied in excess, and with the fire low and open in the firebox, the temperature is gradually raised to about 500° C., when the reactions of roasting take place. The temperature must be moderate to avoid fusion, which would coat the particles with a layer impervious to air and cause them to stick together, in both ways interfering with the roasting. The ore is stirred and mixed by means of iron paddles to expose it to the action of the air and heat as freely as possible without turning under any burning sulphur and to break up any lumps that may have possibly formed. It is aimed to oxidize only a portion of the lead sulphide, leaving the balance to carry out the reactions of reduction. When it is judged from previous experience that sufficient oxide (and sulphate) have been formed for this purpose, the firebox is filled with fresh fuel, the air supply is cut off or diminished, and the temperature gradually raised until the charge becomes somewhat pasty. In this state the reactions

of reduction take place to the best advantage. As soon as it is established, metallic lead begins to flow to the depressed part of the hearth; the charge is worked with iron rakes to bring about a thorough mixture and insure contact between the lead sulphide and the oxides formed and also to liberate any lead that has been reduced and is mechanically retained. This is continued until lead ceases to flow. The lead in the depression of the hearth is then tapped, through a notch arranged for it, into an iron pot outside, where it is skimmed with a perforated skimmer. The skimmings are set aside to be added to the next charge and the lead is dipped out with a ladle and cast into bars.

42. Second Run.—By this time the charge is pretty soft and a small amount of lime is thrown upon it to stiffen it. The lime may also reduce a small amount of lead sulphide to lead, as indicated in the reaction in Art. **8** (though this action is unimportant). After being worked a short time, coal slack is thrown upon the mass, which is again heated to reduce any lead oxide that may have been formed in excess. The mass is worked in until no more lead is obtained.

The second run is of inferior grade, containing any metallic impurities that may be present in the ore in much larger amounts than the first run. It is known as **slag lead** and is usually kept separate to be subsequently refined. The slag is drawn through the working doors of the furnace by means of rakes and is allowed to cool, after which it is removed to the slag dump.

43. Effect of Foreign Materials.—The effect of foreign materials on reverberatory smelting may be disregarded if the ore contains 80 per cent. or over of lead. Pure galena contains only 86.6 per cent., so that the amount of injurious elements in such a case could not be very large. An ore of this grade, however, is very rare and the average of the ore treated by the reverberatory method is, perhaps, nearer 70 per cent. of lead. In this case the influence exerted by the gangue and associated minerals should be counted

upon. The prime essential is that the ore should run high in lead. The separation of the lead from the slag is at best incomplete on account of the mere mechanical retention of shots in the pasty mass; also if slag lead is not extracted, much may remain in the form of lead oxide.

44. Pyrite, in general, seems to favor the oxidation of the galena in the first or roasting stage, both mechanically and chemically; mechanically by making the charge looser and chemically by the action of the sulphur trioxide SO_3 produced by the oxidation of the iron sulphide FeS_2 to iron sulphate $FeSO_4$ and the subsequent decomposition of the latter. But if too much pyrite is present, it interferes with the reaction in the reduction stage by mechanically diluting and keeping apart the oxidized and unoxidized galena. It is also liable to form matte, retaining some lead and interfering with the tapping on account of its fusibility. From 10 to 12 per cent. of pyrite is objectionable, and it is impossible to smelt by this process ore containing as much as 40 per cent. FeS_2.

Chalcopyrite has, in general, the same effect as pyrite, but is somewhat more objectionable because the copper alloys with the lead to some extent and thereby contaminates it.

45. Zinc blende, being quite infusible, assists mechanically in the roasting stage. It has little or no chemical effect in the reduction stage, but interferes mechanically if too great an amount is present. As in the case of pyrite, 10 to 12 per cent. of blende is bad and 40 per cent. stops the operation entirely. It is further objectionable because of its effect on silver. Some metallic zinc is inevitably reduced in the second stage; this volatilizes and mechanically carries with it more or less silver.

46. Antimony is usually present as some form of sulphide. It is especially objectionable for the following reasons: It is fusible both as a sulphide and as a metal, and

thus causes the ore to cake and interfere with the roasting. It combines with both lead sulphide and lead oxide, forming readily fusible compounds, easily volatile, and of such a character that they remain in the slag. All forms that occur in the furnace, including the metal, are easily volatile; and by their volatilization cause losses of lead and silver. Whatever is reduced to a metallic state and remains unvolatilized appears in the lead, making it hard and impure.

47. Arsenopyrite.—The arsenic contained in **arsenopyrite** acts in a manner similar to antimony and is nearly as objectionable.

48. Silica readily forms silicate of lead, which, on account of its easy fusibility, coats the ore, thus making it pasty and lumpy and causing it to adhere to the hearth and tools; it, therefore, interferes seriously with the roasting. Lead silicate when formed goes into the slag. If the slag is subsequently treated in a blast furnace for the recovery of its lead, this last objection is not so serious. Very small amounts act deleteriously, but the statement that 5 per cent. stops operations altogether appears to be unfounded.

49. Limestone in small amounts tends to keep the charge stiff and does not interfere with the process in either stage; it is therefore not undesirable, but if added to the charge in too great amounts it will interfere mechanically. The action of lime in the process of extracting slag lead is probably more mechanical than chemical.

50. Lead Products.—That which first flows in the reduction stage is known as **virgin lead** and contains most of the silver with comparatively small amounts of other metallic impurities. The slag lead has already been mentioned; the farther its extraction is pushed, the greater is the amount of impurities that it will contain. If this amount is large, refining may be necessary.

51. Slag consists of the residue, that is, the gangue and such impurities as have not been volatilized or carried off by

the lead together with any lime or coal ash that may have been added more or less fused together. In composition this is very uncertain. The amount of lead in slag depends on the completeness of the extraction of the slag lead. If this has been pushed to the limit, the lead in the slag should not run over 5 per cent. If no extraction from slag lead has been attempted, the amount of lead may be as high as 50 per cent. If the slag is high in lead and especially if it contains any considerable amount of silver, it will undoubtedly prove desirable to resmelt it in the blast furnace, where a much closer extraction is effected.

52. Secondary Products.—It has been noted that lead, lead sulphide, zinc, arsenic, antimony, and the compounds of lead with the two last-named are volatile. This fact gives rise to losses that form a serious problem in lead smelting. Whatever method may be adopted, not only do the substances named volatilize directly, but the fumes mechanically carry with them fine particles, and the losses in silver from this cause sometimes run high. There is also a certain amount of fine fuel and ore dust carried away by the furnace draft. Taken in the aggregate, these losses form an appreciable and important item. To effect their recovery, it is customary to pass the waste gases through long horizontal flues, to allow the materials carried by them to settle out. The dust collected there is known as **flue dust.** It is occasionally collected and added to the charge in the reverberatory furnace; sometimes it is smelted with the slag in the blast furnace. The temperature at which reverberatory smelting is conducted is much lower than that of the blast furnace and the losses by volatilization are proportionately smaller, but if much lead is being smelted, the fume is well worth saving.

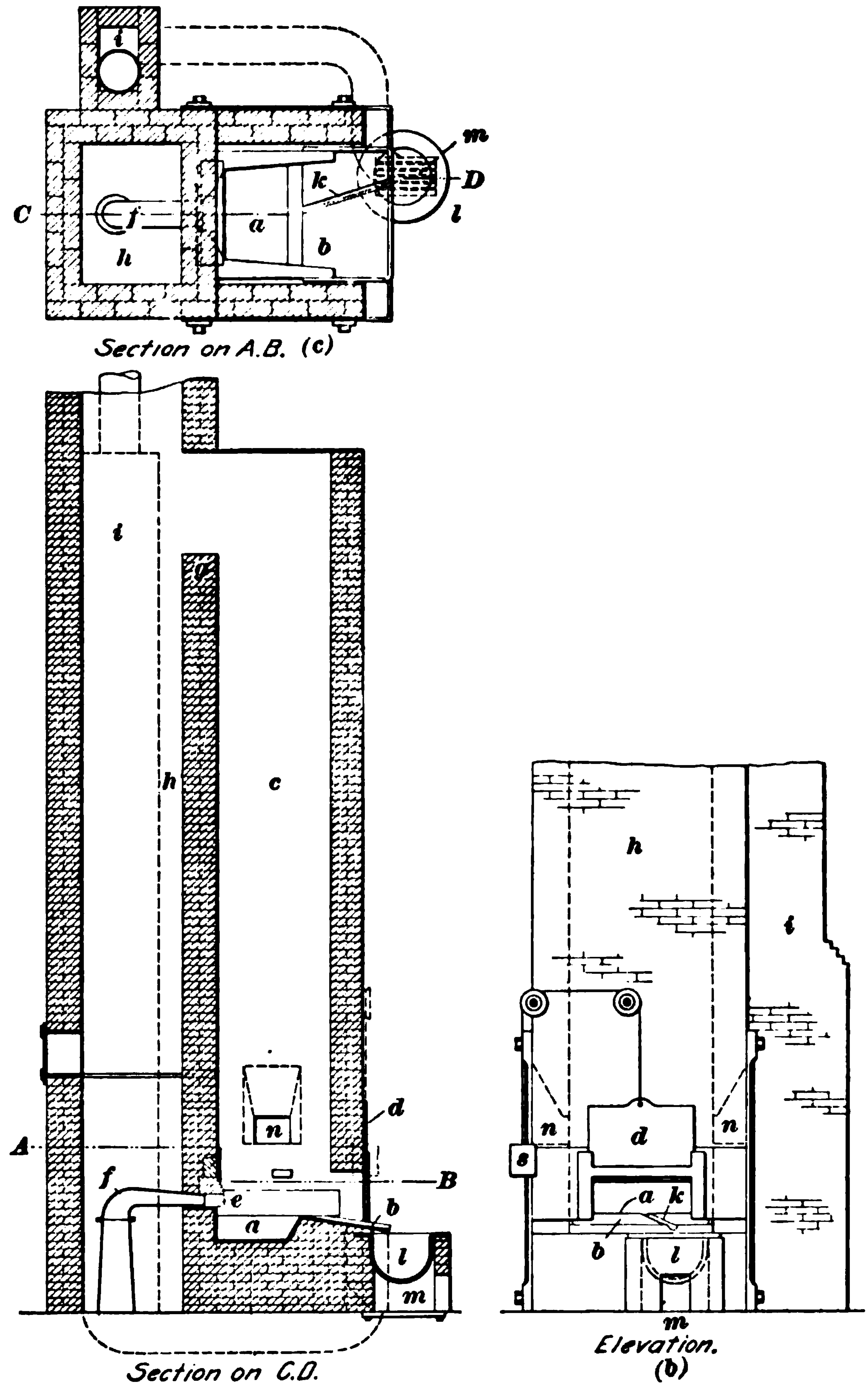
The hearth of the reverberatory furnace in time becomes saturated with lead and lead compounds. When worn out, much lead will probably be found there; and if the ore smelted has been argentiferous, it is likely to be especially rich in silver. This is also smelted in the blast furnace.

ORE-HEARTH SMELTING

53. Description of Ore Hearth.—Smelting in the ore hearth is similar in many respects to reverberatory smelting, at least, so far as the chemical reactions are involved. The limitations as to the quality of ore that may be treated curtail its usefulness, yet, because of the low cost of the plant and its possibilities in isolated regions, a short description of the process is given here.

The ore hearth is essentially a cast-iron basin *a*, such as is shown in Fig. 3, rectangular in shape, with a lower front than back, and terminating in an apron *b*. This is set in a brick shaft *c* provided with a door *d* over the apron. At the rear end of the shaft, over the basin, is an opening *e* for the blast pipe or tuyere *f*, which is directed slightly downwards into the basin. The shaft is divided into two partitions by a brick wall *g*, which causes the gases to rise and then to pass downwards through *h* before entering the chimney *i*, shown by dotted lines. The fumes collect in this shaft *h*, the only purpose of which is the recovery of fumes; this is necessary both to protect the health of the furnacemen and to recover the lead that may be volatilized. In operating, the basin is kept full of molten lead, and on its surface float the ore and the fuel, which are thus raised to the level of the air blast. The molten lead serves as a protection for the cast-iron basin, and it would be difficult to devise any more effective support for the ore in the process of smelting. As fresh lead is reduced from the ore it descends through the charge to the basin, and a corresponding amount overflows upon the apron *b*, which is known as the **work stone.** This slopes away from the basin, as illustrated in (*a*), and is provided with a groove *k*, Fig. 3 (*c*), to carry the lead thus overflowing to the kettle *l*.

54. Ore-Hearth Practice.—The operation of the hearth is as follows: Two men are required and a shift lasts 8 hours. The fuel is coal and peat cut in prismatic pieces from 9 to 12 inches long by 2½ inches square. The ore need not necessarily be calcined and the blast should be


i
m
k
D
C
f
a
l
h
b
Section on A.B. (c)
i
h
c
d
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B
f
e
b
a
l
m
Section on C.D.
(a)
h
i
n
d
n
s
a
k
b
l
m
Elevation.
(b)

FIG. 8

varied considerably to agree with the nature of the ore operated on. The hearth in this description is supposed to be in working order and the bottom to be nearly full of lead. A small quantity of coal is laid on the hearth bottom and the remaining cavity of the hearth is filled with peats, which are well walled up in front, while smaller pieces are thrown in behind without order. A few ignited peats are next placed before the nozzle and the blast turned on. As soon as all the peats are well ignited, a little more coal is added and shortly afterwards a little of the slag from the last shift is thrown on behind the work stone. When about half of the slag is worked in, lead begins to flow; then one of the workmen stirs the contents of the hearth with a poker, throwing it forwards from the blast, a portion falling on the work stone. At this moment the other workman introduces his scraper through the feed-door *n* and removes any slag from before the blast, throwing in front of the nozzle a peat, which disperses the blast and keeps open the fire. Both men then step to the front with their slag shovels and put back into the hearth what has fallen on the work stone, setting up the contents so that the blast will be well distributed throughout. Lead now flows freely. Ore in small quantities is added where the fire seems hottest. The stirring of the contents of the hearth is repeated at intervals of about 5 minutes, where the fire is seen to burn badly on account of the imperfect diffusion of the blast. At each stirring a fresh peat is placed in front of the nozzle, and from the portions that, during this manipulation, fall upon the work stone, lumps of gray slag are picked out and laid aside for subsequent treatment in the slag hearth. The pieces of slag are broken up and returned to the hearth, after which fresh ore is added. When the receiving pot *l* is full of lead, the latter is skimmed and laded into pig molds. During a shift these operations of stirring, lading, etc., are performed alternately by the two workmen. Thus, the man who has been using the poker lades out the metal while the other skims it; and the latter attends at the feed-door while the former uses the poker. Towards the end of the shift no

more ore is charged, but the contents of the hearth are afterwards worked up two or three times, after which the blast is stopped. All the sintered ore is taken out, thrown to one side, and separated from the intermingled gray slag. Lead is laded from the receiving pot back into the hearth bottom, so as to fill it ready for the next shift. A small fire is kept on the grate *m* under the kettle *l* to keep lead liquid.

55. American Ore Hearth.—The ore hearth proper naturally does not admit many modifications; the following, however, may be mentioned: In the Scotch ore hearth shown in Fig. 3 the basin is enclosed in solid brickwork. It is about 2 feet from front to back, 1 foot 9 inches wide, and 1 foot deep, and contains about 1 ton of lead. After working from 12 to 15 hours this hearth gets so hot that the

Fig. 4

volatilization of lead becomes excessive and work must be stopped long enough for the hearth to cool. For this reason Americans made the two modifications shown in Fig. 4. In both, the sides and back above the basin were hollow iron boxes *a*, as shown in the illustration. In the first the air for the blast was forced through these boxes, thus cooling them. The blast, however, was so heated by this means that the temperature developed in front of the blast nozzles was

excessive and the volatilization of lead continued. The second modification was, therefore, introduced. This consists of cooling the sides and the back by allowing water to flow through them. The blast being cold, this form gives the results desired and can be used continuously. It has been found desirable to have three tuyeres *b*, instead of one. The work stone *c* slopes to a cast-iron pot *d*, under which a fire is kept to prevent the metal coming from the furnace cooling before it can be ladled out. A similar arrangement is shown at *m*, in Fig. 3. Wood is used as fuel, both on account of convenience and because it has been found that coal or coke are too concentrated in form and produce too concentrated a blast. In the illustration, *e* represents the molten lead and slag and *f* the wood and the ore not yet melted. The door through which the workmen manipulate the charge is not shown in Fig. 4.

56. Recapitulation.—Impurities have, in general, the same effect in ore-hearth smelting already noted for reverberatory smelting. The ore should be in pieces not less than ½ inch in diameter, with as little fines or dust as possible. The losses of lead due to volatilization are much greater in ore-hearth smelting because the heat is concentrated in front of the tuyeres. The slag produced is a heterogeneous mixture and runs very high in lead, as might be expected. For any economy in working, it should afterwards be resmelted in some form of blast furnace. When the ore hearth was used in the United States, a low shaft furnace, known as the **slag-eye** furnace, was used for this purpose.

The ore hearth requires considerably less fuel than the reverberatory, but on accouut of the cost of power and labor and the small output that is possible, it cannot compete with it in the cost of production. Its chief value lies, therefore, in the fact that it can be readily started and stopped and can be used in isolated localities. At the present day, when railroads have made accessible nearly all regions of any importance as sources of lead, the utility of the ore hearth in this country has practically disappeared.

BLAST-FURNACE SMELTING

57. Ores for Blast-Furnace Smelting.—It is to be understood that only ores of the purest grade and highest percentage in lead can be smelted by the processes described; also that it is practically impossible to mix "dry" ores of gold and silver with lead ores and smelt them by these processes. They are, therefore, far too limited in their application, and resort must be had to the other alternative made possible by the nature of lead and its compounds, namely, first roasting the ore to remove the sulphur and to convert the sulphide of lead into lead oxide or silicate and then reducing these compounds of lead to a metallic state in the shaft furnace. At the same time, everything charged into the furnace is fused, to be separated subsequently while still in a molten condition by reason of the difference in the specific gravities. By such a process, ores containing as low as 10 per cent. of lead may be successfully smelted, and a much closer recovery of lead can be effected, while the deleterious effects of the impurities may be much more readily counteracted. If the ore is a carbonate, no preliminary roasting is required; but carbonates are becoming more and more scarce, and at present about one-half of all the ore going through the blast furnace requires roasting to eliminate sulphur. If arsenic is present, it may be partly removed from the ore in the process of roasting, which is a decided advantage.

58. Roasting Lead Ores.—The theory and practice of roasting, with the chemical processes involved, have already been fully discussed, but it seems desirable to make some comments here upon its special application to lead ores. They differ from most other ores in their easy fusibility and volatility, and a process that would work admirably with copper ores might prove quite fatal to a successful handling of lead ores. On account of the perfect control that it is under, regarding both the handling of the ore and the temperature, the old well-known type of long-hearth, reverberatory roasting furnace, in which the ore is rabbled and

moved forwards by hand entirely, is still the standby for roasting lead ores. In this furnace, the ore in the preliminary stages of roasting can be allowed to remain more nearly undisturbed as long as may be necessary to allow the sulphur to burn off; if a particle of ore is turned under while the sulphur it contains is still burning, it causes caking and a consequent hindrance to the elimination of the sulphur. On the other hand, when the roasting process is nearing completion, the ore can be turned and mixed as often as may be desirable to expose it to the full oxidizing effect of the furnace, so as to obtain a complete removal of sulphur.

Again, it would be decidedly bad to move forwards any raw sulphide ore to a part of the furnace where it would be subjected to sufficient heat to bring about a reduction of lead by its interaction with oxidized ore, such as takes place in the reverberatory smelting process. This is much less liable to take place in a hand roaster than in a mechanical furnace, where raw ore has a chance to stick to the rabble. It is possible, also, to roast the ore closer, because the time when it is finished is judged by a man who should be experienced in such matters, instead of being left entirely to mechanical devices. The amount lost in flue dust and by volatilization should be very much less if hand rabbling is properly done. It is practical and customary to give the ore a final high heat just before its discharge from the hand reverberatory, which at least sinters it together and may fuse it entirely, thus sending it to the blast furnace in lumps instead of as fines. Fine ore is objectionable, and in the mechanical roasting furnace such sintering or fusion of the ore is impossible. Finally, the original cost, the expense of maintenance, and the care necessary to mechanical roasting furnaces are avoided. The great drawback is the much larger amount of labor required; and this one point is so serious that most lead smelters at present use both hand and mechanical roasting furnaces. If any difference exists, the mechanical furnaces usually take the subordinate place. There are plants equipped exclusively with hand roasters, but none so equipped with mechanical roasters.

59. Mechanical Roasters.—As already suggested, operating mechanical furnaces when roasting lead ore is quite a different matter from working the same furnaces on copper ore. The heat must be much less intense and the ore must be moved up to its highest temperature more slowly and with less frequent stirring. As an instance, in the Pearce turret furnace, as a type of roasting furnace with stationary hearth, the firing is much less intense; and where the rabble arms would make a circuit of the furnace once a minute for copper ores, they make but one circuit in 10 minutes for lead ores, and this where but one pair of arms is used, the second pair being retained for use in case of accident.

Corresponding changes are necessary in the running of other stationary hearth furnaces that are used in roasting lead ore, such as the Ropp straight-line furnace, the Brown horseshoe furnace, and the Allen-O'Hara furnace. The Brückner cylinder furnace, as a type of movable hearth furnace, is run very slowly indeed; where 12 revolutions per hour would be made in roasting copper ore, but 1 revolution in 40 minutes, and in extreme cases even as low as 1 in an hour, is made for lead ore. The Brückner cylinder has a decided advantage over the stationary hearth type of roasters, because in it the ore is charged all at once and the heat as well as the frequency of stirring can be regulated to suit exactly the condition of the ore. It roasts closely, and these advantages seem to be recognized by lead smelters, for the Brückner furnaces are being introduced more widely at the present time than any other type of mechanical furnace. Its great drawback is the amount of flue dust formed; but even this is diminished by the slow rate of revolution.

It might be well to note here that the introduction of a steam jet at the firebox end of the Brückner cylinder is quite common and is found very effective in introducing fresh air for the oxidation of the ore and the removal of the sulphurous gases so formed.

To sum up their advantages in a very few words, mechanical furnaces in general give very fair results as to closeness of roasting, with very low labor cost.

60. Slag Roasting.—One point in connection with roasting in hand reverberatories that should be given some consideration is whether the ore should be merely sintered together at the end of the roasting or completely melted down. The latter practice is termed **slag roasting,** which has for its objects the elimination of sulphur and the agglomeration of fine ore into lumps. Lump ore is better suited to blast-furnace practice than fine ore. The elimination of sulphur is effected according to the reaction

$$2PbSO_4 + SiO_2 = Pb_2SiO_4 + 2SO_3$$

To bring this about, if sufficient silica is not already present in the ore, a small amount of fine sand is added to the ore, and it is brought forwards to that portion of the hearth nearest the firebox, which is contracted in width and is some inches lower than the rest of the hearth. Here the heat of the firebox is concentrated by the narrow hearth, and by having the roof somewhat lower the ore is soon melted

FIG. 5

down with the evolution of sulphurous or sulphuric anhydride. The melted material is then drawn by rakes into iron pots of conical shape mounted on wheels, as shown in Fig. 5, and allowed to cool. The sintered ore is then dumped, as shown in Fig. 6, after which it is broken into large lumps by means of a sledge hammer, to make it handy for charging into the blast furnace.

61. Objections to Slag Roasting.—The drawbacks to this practice are the high losses in lead and silver and the

extra labor required for handling the ore in the **fuse box,** as the contracted portion of the hearth is called. The first-mentioned objection is so serious that in most cases the method has been abandoned, and the ore is only heated to a point where it sticks together in more or less coherent lumps. The sulphur is not removed quite so closely, because the reaction between the lead sulphate and silica takes place to a very limited extent, if at all. But it is reduced low enough for all practical purposes, since there is some elimination of sulphur in the blast furnace itself, and furthermore,

FIG. 6

if any copper is present, it is desirable to have it appear in the form of matte rather than as metallic copper, and for this purpose a corresponding amount of sulphur will be necessary. As to obtaining the ore in lump form, it is found that if the roasted ore that has been slightly sintered is drawn into the same pots as those used for receiving the slagged ore and rammed down firmly and then one or two holes punched in the mass to allow the escape of any gases, it will adhere sufficiently to stand the handling necessary before charging.

62. Ore Mixtures.—As to the limit between ore that requires roasting and that which does not, no arbitrary line can be drawn. The object aimed at is to reduce the average percentage of sulphur in all the ore charged into the blast furnace at one time to a figure that has been found by practice to be desirable. To do this, it may be possible to mix in the charge without roasting a small amount of raw ore running quite high in sulphur, but also rich in silver; while an ore somewhat lower in sulphur, but also poorer in silver, that appears in much greater amount in the charge, will be roasted to bring down the average sulphur contents. In general, the higher the silver contents of the ore, the less desirable it is to roast it, on account of the inevitable loss due to volatilization; and it is usually thought satisfactory if the average of the sulphur in the total amount of the ore charge is 4 per cent., or less.

63. Furnace Charges.—The first step in the consideration of actual blast-furnace smelting should be to gain a clear idea of the results aimed at and the methods that might be used to attain them under the simplest possible conditions. Suppose, then, that the ore to be smelted contains 20 per cent. of lead oxide and that the other 80 per cent. is made up of ferrous oxide, lime, and silica in such proportions that they will combine under the influence of heat to form a compound readily fusible at the temperature of the lead blast furnace, and differing sufficiently from molten lead in its specific gravity to separate readily from it. If this ore be charged into a properly constructed shaft furnace with alternate layers of coke, amounting to, say, 15 per cent. of the weight of the ore (the coke ash is assumed to be low enough in amount to have no appreciable effect upon the composition of the slag) and the amount of cold air to be blown in at points near the bottom is such that the coke is burned mainly to carbon dioxide, reducing all the lead oxide and none of the ferrous oxide to metal, the highest temperature will be reached at a point just above where the air blast is admitted and the entire charge there

will be brought to a molten condition. The products of combustion will pass off through flues, while the lead and slag will descend to the bottom of the shaft and there collect in two layers—the lead at the bottom, the slag at the top. As the level of the slag rises nearly to that at which the air blast is admitted, the lead and slag may be partially tapped out through two separate tap holes constructed for the purpose. More ore and fuel being constantly charged above, the descent of molten lead and slag will continue and the *blast-furnace smelting* will be in operation. Of course the conditions just described are ideal and are never reached in practical work; but they are approximated as nearly as possible. To bring about the desired conditions many details in construction and operation must be calculated very closely.

Fig. 7

LEAD BLAST FURNACES

64. In Fig. 7 is shown the partial cross-section of a lead-blast furnace. In the figure, *a* is the crucible, *b* the water-jackets, *c* the tuyere pipe, *d* the canvas air pipe connecting the tuyere *c* and bustle pipe *l*. Above the bosh *g* is a lining of firebrick *h*, which is carried up to the charging door *k*. In the section, *i* is termed a lead siphon.

In lead smelting, the aim is to effect the smelting at as low a temperature as is consistent with keeping the furnace open and obtaining slags sufficiently fluid to give a clean separation from the lead. It is desirable, therefore, to concentrate the heat and to limit the zone of chemical action. Any height of the furnace above that necessary to obtain the full chemical and calorific effect of the fuel and products of combustion is consequently a loss. Greater blast pressure will be required to force the air through the lengthened column of ore and fuel without any compensating gain or advantages whatever.

65. The shape or horizontal cross-section of a rectangular lead blast furnace is shown in Fig. 8. In the figure, *a* are tuyere openings in the water-jacket *b*, which is made in sections and bolted together by lugs, bolts, and nuts *c*. The hearth frame is represented by *d* and the furnace legs by *l*. In horizontal section the lead furnace is built either circular or rectangular.

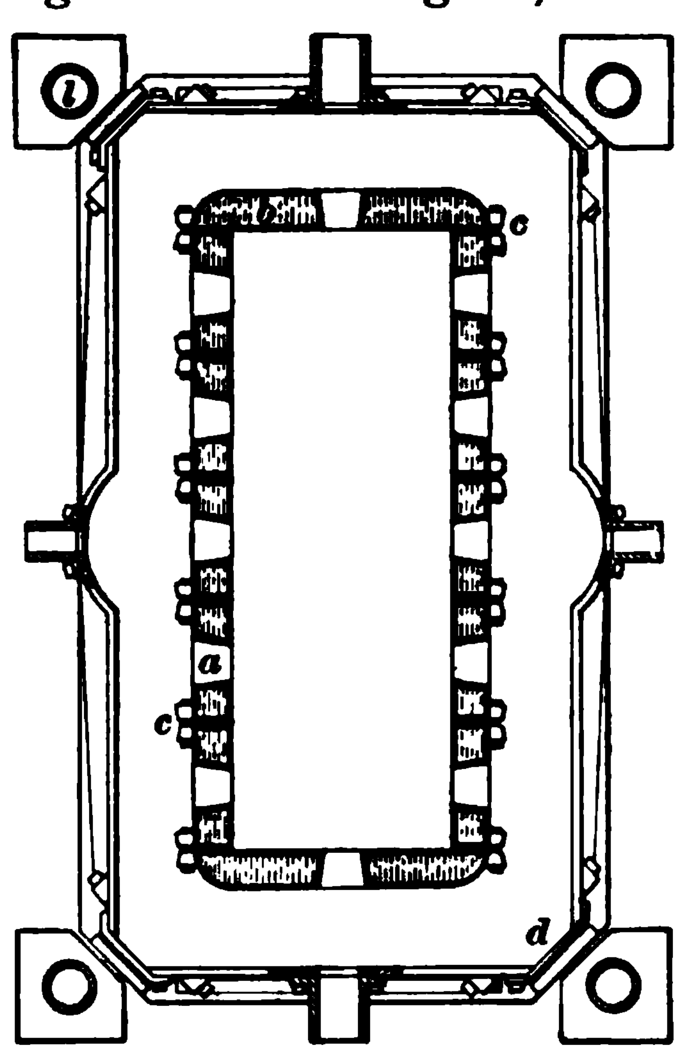


FIG. 8

The size of the circular furnace is limited by the fact that it is undesirable to use blast pressure above a certain point. If furnaces are increased in diameter to such a point that this air pressure is not sufficient to penetrate the center

of the charge, the combustion of the fuel will be incomplete and imperfectly smelted ore will go past the tuyeres down into the crucible and cause considerable trouble. It is impossible, therefore, to enlarge the furnace with circular cross-section beyond this limit, which should not exceed 48 inches from nozzle to nozzle of opposite tuyeres. The only way to increase the capacity of the furnace, then, is to make it rectangular in cross-section and of a width not exceeding the limit just mentioned. It may, however, have a length to which there is no theoretical limit, but which up to the present time has in practice been confined to 160 inches.

66. Zone of Fusion.—In vertical section (Fig. 7) the furnace is narrowest at the crucible *a*, gradually expands above the tuyeres *c*, and is widest at the bosh *g*. The object of this contraction and expansion is to concentrate the effect of the blast in a narrow zone. As the heated gases rise, they expand gradually above the tuyeres until they reach the bosh, thereby decreasing their velocity; and by coming into contact with the charge, give up their heat. By this arrangement the zone of fusion is contracted to a narrow limit, so that the lead and slag go from this point to the lower portion of the furnace at a temperature sufficiently high to secure their liquidity. The charge does not become excessively heated before it reaches this point, and thus a **hot top** is avoided. In general, the ratio of the area of the cross-section at the tuyere level to that at the top of the furnace is 1 : 2 or 1 : 2½. In rectangular furnaces the expansion may take place at the sides or in both sides and ends.

67. Blast Pressure.—The areas of the largest silver-lead furnaces so far constructed are 48 by 160 inches, inside measurements of the crucible. Usually the tuyere nozzle is made flush with the sides, as shown at *b*, Fig. 7, but in some instances water-cooled tuyere nozzles have been projected into the furnace to a distance of about 6 inches. In such a

case, a distance of 48 inches between tuyeres being still maintained, the consequent total width of the furnace is enlarged to 60 inches or thereabouts. In height, the present tendency is to increase the size of the blast furnace, as already noted, with a corresponding increase in the pressure of air. The old-style furnaces, operating under a blast pressure of from 8 to 12 ounces per square inch, had a height possibly 10 or 12 feet, from tuyere level to feed floor *k*, Fig. 7;

FIG. 9

but as slags containing less iron were found desirable, both from a financial standpoint and on account of their clean separation from lead, it became necessary to increase the blast pressure, so that now from 1.5 to 2 pounds pressure is used and in some cases exceeded. Greater height has been given to furnaces to meet this requirement and to economize in fuel; so that 20 feet is perhaps a more representative figure for present practice than any other.

CONSTRUCTION OF BLAST FURNACES

68. Bed for Furnace.—The foundation is, of course, of the first importance; since it has to carry heavy weight and little or no settling must take place or cracks in the shaft will result. The foundation is usually constructed of masonry or concrete, as shown at *e*, Fig. 7, or by pouring molten slag from a blast furnace already in operation into a

FIG. 10

pit. Upon the top of the foundation, as thus prepared, is placed a boiler-iron plate for the purpose of keeping lead that may leak through the crucible of the furnace from passing into the foundations. Upon this bedplate are erected four cast-iron columns *a*, shown in Fig. 9, which carry the brick shaft of the furnace. The steel arch girders *b* are held in place, as shown, by the rods *c* and the side

girders *d*. These latter are sometimes water-jacketed to prevent their burning out when the brick lining that they carry has burned thin.

69. Furnace Crucible.—The crucible of the furnace is shown in process of construction in Fig. 10. It is constructed entirely of firebrick *a*; in some instances these are laid directly on the iron bedplate, in others on a course composed of a mixture of ground brick and clay. In any case, the layer of firebrick forming the bottom of the crucible should be laid in the form of an inverted arch, so that if any

Fig. 11

lead should leak through, it would not be possible to force up the firebrick bottom. The walls of the crucible are constructed very thick; in this way the heat of the lead is retained and danger of chilling or freezing the hearth is avoided as far as possible. The crucible is strengthened by iron plates *b* bolted together, as shown in Figs. 10 and 11, which may be further reenforced by ribs or by bands passing entirely around it.

70. Brickwork.—The brickwork composing the shaft above the girders is shown in Figs. 7 and 11. The inside of the stack is lined with firebrick, while the shell is composed of red bricks, usually bound together at the corners by means of angle irons and tie-rods, as shown at *a* and *b*, Fig. 11. The bricks rest on the plates and cross-ties, and to prevent thrust, the girders are firmly bound together, as shown at *c*, in Fig. 11. The thickness of the walls of a furnace stack is greatest at the bottom, possibly 40 inches, decreasing towards the top of the shaft to about 18 inches. The height of such brickwork is about 20 feet above the tuyeres in large furnaces running on strong blast pressure.

71. Water-Jackets.—It was customary at one time to use a firebrick lining in blast furnaces of this description, but the corrosive action of the molten lead was so destructive that after experimenting with various refractory firebrick linings the water-jacket was adopted for that portion of the furnace above the crucible. The water-jackets rest on the crucible walls, as shown in Fig. 7, and have a portion of the stack brickwork resting lightly on them, as shown at *g*, in the same illustration. A section showing a water-jacket through the tuyere hole is given in Fig. 12. Recent improvements in water-jackets is a partition dividing them into two sections, as shown in Fig. 13. Section *a* is for the water-jacket and section *b* for the air blast, which enters through the flange *c* at the top of the jacket. The blast becomes heated in chamber *b* and enters the tuyere *d* direct.

FIG. 12

FIG. 13

The tuyere hole *f* is 4 inches in diameter and is closed with a taper plug *g*, which can be removed quickly for the insertion of a bar, in case the tuyere should become closed by the furnace charge. This plug is provided with a sight hole *h*, for the purpose of looking into the furnace and ascertaining if the smelting is progressing favorably.

72. Cast-Iron Jackets. — Water-jackets are usually made of cast iron, wrought iron, or steel. If of cast iron, they are made in sections, each section containing the opening for one tuyere; if of steel, generally but four sections are used for the entire furnace—two for the sides and one front and one back. In cases, however, where it is necessary to have everything made in sections for transportation by pack animals, steel jackets in sectional form are especially desirable on account of the possibility of making each section so much lighter than a corresponding iron one, in addition to the other advantages. The cast-iron jackets are about 6 inches thick and have walls averaging ½ inch thick. Inlets and outlets for water are at the tops of the jackets and extend above them, to insure the jackets remaining filled; the cold water flowing in sinks to the bottom, because of its greater specific gravity, and as it becomes heated rises to the top and overflows into a trough that carries it away.

Cast-iron jackets cost, as a rule, from one-third to one-half as much as steel jackets; they are, therefore, desirable types to use when the smelter is near an iron foundry or can get cheap freight rates. In practice, under such conditions, the cast-iron jackets are always used. The steel jackets are more economical for regions at a distance from the foundry and where high freight rates prevail, being both lighter and more durable. Where they are made in four sections only, that is, one section for each side and end, they are so long that they must be braced from the inside to prevent bulging. This necessitates riveting the braces on the fire side, which is an objectionable feature. Undoubtedly the better way would be to have them made in 20-inch sections; as in the case of the cast-iron jackets; they should then give

excellent service, with proper care. Cast-iron jackets were formerly made in a number of different patterns, to provide for the complete enclosure of the crucible. More recently

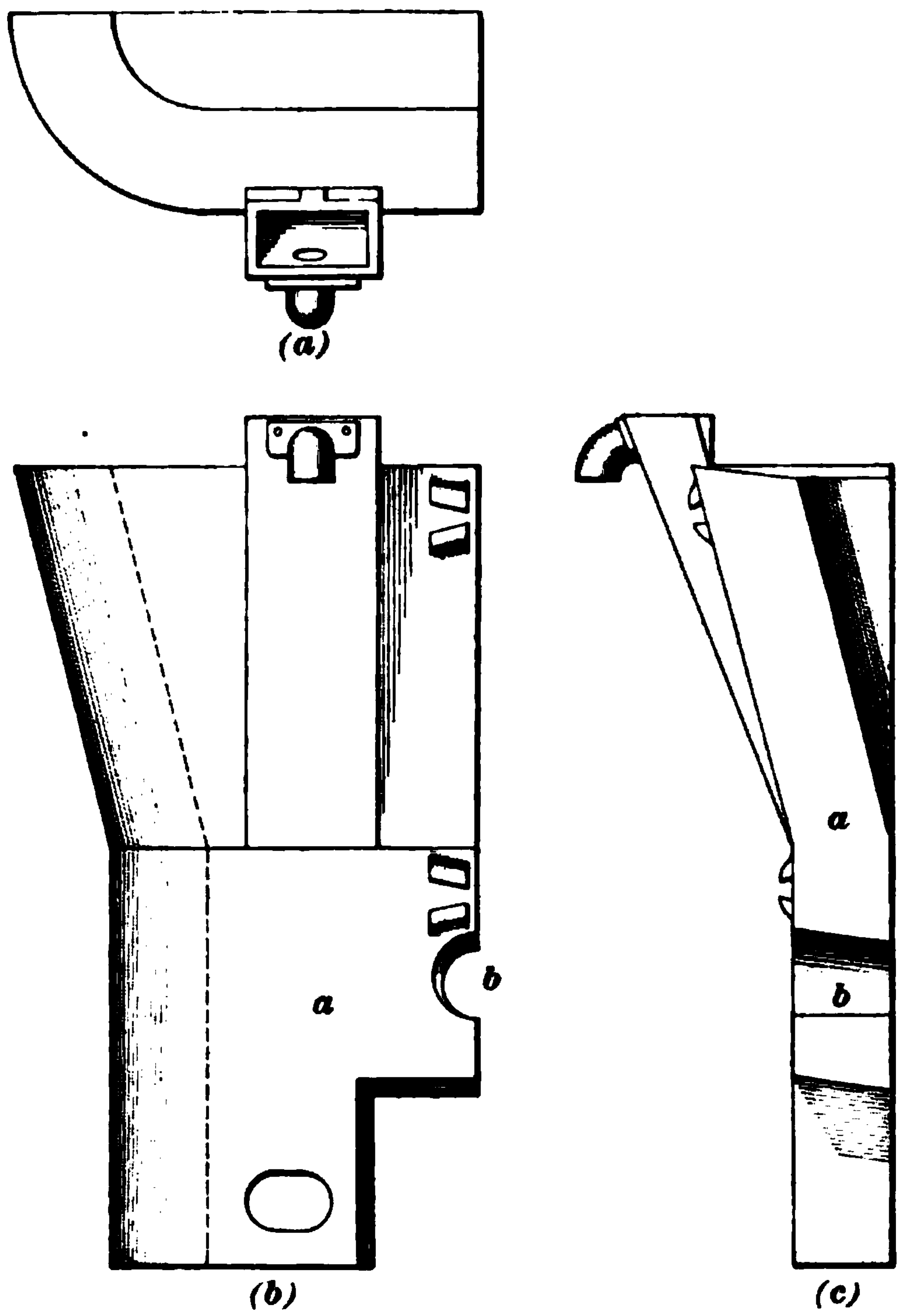


FIG. 14

the number has been reduced by making one type for use on the sides and a curved (right- or left-handed) one, as shown in Fig. 14, for use at the corners, and a third type for use in the front or back.

73. Tapping Jacket.—The two front jackets are so arranged as to allow the insertion of the tapping jacket, as shown at *a*, in the illustration Fig. 15. The tapping jacket has a notch *b* penetrating it, through which the slag is tapped; this notch is circular in section parallel to the face

Fig. 15.

FIG. 16

of the jacket, and increases in diameter from inside to outside—in other words, it has the shape of a truncated cone, with its smaller base inwards.

Above the tapping jacket a small space is left in order to make the withdrawal of the jacket easy, in case it becomes necessary to get at the interior of the crucible. In some cases it is arranged to extend the space several inches below the upper edge of the crucible in order to prevent the leakage of molten lead at this point, which is usually weak. A good illustration of the space left for a separate cast-iron water block, slag spout, and tapping jacket is shown in Fig. 10. The object of the separate cast-iron water block is to prevent the brickwork being cut out, as it certainly would be if any leak should occur. Above the water-jackets, firebrick is built in to fill the space between them and the shaft proper. The jackets may or may not carry part of the weight of the firebrick lining above them, this point depending on the construction of the support of the shaft.

In Fig. 15 the method of strengthening by bolting the crucible is shown, as well as other particulars not hitherto illustrated. In the figure, *a* is the tapping jacket, *b* the slag notch, *c* the crucible, *d* the water-jacket, which is fed from the water pipes *e* by water passing through 1-inch pipes *f* into the top of the jacket. The trough *g* that receives the water after it is discharged from the jacket is also shown. The pipes *h* shown in the front of the furnace supply the tapping jacket with water. The bustle pipe *i* is shown in place, also the blast pipes *d*, the canvas pipes *k*, and the tuyere pipes *l*. The method of supporting the bustle pipe, pillars, framework, and arch for the brick furnace stack is also shown.

CHARGE OPENINGS AND REMOVAL OF GASES

74. Feed-Doors and Flues.—The arrangement of feed-doors and flues at the top of the shaft is according to one of three methods. In the first instance the shaft shown at *a*, Fig. 16, terminates with the feed floor, which is covered

with iron plates. An opening about 2 feet wide and varying in length with the length of the furnace is left in the feed floor. Through this opening, ore, fluxes, and fuel are fed into the furnace. The gases are removed by means of a brick flue *b*, built at one end, near the top, as shown, and slightly inclined downwards to connect with the main flue. This offtake, termed a **down comer,** usually has sufficient draft passing through it to prevent the furnace gases passing through the feed opening into the charging floor. The air-current is rather in the opposite direction; a moderate amount of air passing through the feed opening dilutes and cools the furnace gases to some extent. As the draft is under the full control of the operator, this last feature is in most cases desirable rather than otherwise. If the draft is insufficient to insure the proper removal of the furnace gases, a steam jet is sometimes placed at the entrance to the offtake and is so directed as to carry the gases into it, after the manner of a Körtings jet. Where this arrangement of doors is used, a sheet-iron stack *c* may be suspended above the feed opening to be lowered into place when **blowing in** or **blowing out,** as the operations of starting and stopping the furnace are, respectively, called. At such times the gases must not be allowed to pass into the main flues, since they are liable to contain carbon monoxide CO and might cause an explosion. In such cases a damper in the offtake is closed; the stack is lowered into position and the gases are carried into the open air.

75. The second arrangement is somewhat similar and an arched sheet-iron flue with a very flat curvature passes from the top of the furnace above the feed floor leading to the main flue, as shown in Fig. 17. The third arrangement continues the walls of the shaft directly upwards through the feed floor and out at the roof, contracting with height and forming a permanent stack, as shown in Fig. 7. This is constructed of red brick. The feed-doors are placed in either side of this stack, beginning at or near the level of the floor and extending upwards to such a height as will permit a man

to stand in them to bar down accretions. At the top of the stack is placed a damper. In the ordinary running of the furnace, this damper is closed and the furnace gases are carried off through a sheet-iron downtake that leads from a

FIG. 17

point in the stack well above the feed-doors. It also is provided with a damper, and when blowing in or blowing out this damper is closed and the one at the top of the stack opened. Of these three methods of construction, the third is undoubtedly the best and is being generally adopted. Fig. 17 shows some of the details of such a furnace.

76. Where the opening is directly in the floor, it may be closed, if necessary, by placing over it iron plates similar to those of which the floor is composed. If it is in the side of a stack that is continued up from the shaft, the doors are either hinged at the top and made of sheet iron or they may be made with cast-iron frames fitted with sheet-iron panels running in grooves and suspended from above. In this last

instance it is desirable to have the doors suspended by two chains that pass over a shaft common to both. In this way both sides are uniformly elevated or depressed and jamming is avoided, a difficulty that would frequently occur if the doors were suspended by a single chain. A common feature in the arrangement of the feed openings is to have a ledge several inches high surrounding the openings, so that the man who shovels the charge into the furnace must *lift* it over the ledge, shovelful by shovelful, instead of *pushing* it in without lifting. This is supposed to secure better distribution of the charge, but has been proved unnecessary in at least one instance, the superintendent wisely believing that if a man does not know enough to distribute the charge properly without such a device, he does not know enough to hold such a position with it.

77. Blast for Furnaces.—The air supply in lead smelting is furnished at a pressure that is quite beyond the reach of fans, and custom, apparently, is responsible for the general use of rotary, positive-acting blowers. Of these, the Connersville cycloidal is in most general favor at present; it is

FIG 18

rapidly replacing the Root type, while the Baker has gone out of use almost entirely. In Fig. 18 is shown a positive rotary blower that is driven by a belt. *A* is a pulley wheel for belt, *B* and *C* housings for gears connected with the shafts *c*, *d*, shown in the section. The impellers *a* and *b* rotate in the casing *e* in the direction shown by arrow *V*. The air

is drawn into the casing at *g*, carried half way around by the vanes *a* and *b*, and is discharged at *f*. The impellers are not in contact with each other or with the casing, but are simply a close fit. With the air pressures now used, the leakage in blowers of this type must be very large—by some it is estimated to amount to as much as 50 per cent., though this figure is probably excessive. Lead smelters in general have little or no detailed or accurate information as to the amount of air that is supplied their individual furnaces, and the loss that occurs by leakage of the blowers may amount to a very considerable percentage without being detected. The economy of using a piston blower seems to be a possibility well worth considering. In arrangement, the blowers are usually all connected with a single blast main. This permits the use of a smaller number of blowers than would be necessary if each furnace were supplied by its own blower. In the latter case, provision for breakdowns would require a complicated system of connections, while in the former a few spare blowers connected up with the blast main are all that are necessary. These should be disconnected when idle, to prevent their being run backwards by the air pressure, and so causing a loss of blast.

78. Tuyeres.—Many complicated forms of tuyeres have been devised, but none give better service than the simple type of elbow illustrated in Fig. 15. An opening is left as a peep hole, as shown; this is closed by a wooden plug or a small piece of glass or mica. In case the tuyere becomes stopped, it is easy to remove it and take out the obstruction. The tuyere ports were formerly arranged between sections of the water-jackets, that is, a semi-cylindrical passageway would be left at each side of each section. These, when matched, would make the cylindrical tuyere port. This arrangement was very satisfactory as long as the jackets would match, but if any warping or deformation occurred, the two sides were liable not to match perfectly. The tuyere ports are now made in the center of each water-jacket.

Reference has been made in connection with the width of the furnace to water-cooled tuyere nozzles. This was made

by coiling black-iron pipe 1 inch in diameter around a nozzle that projected 6 inches into the furnace. Through this coil water was circulated and protected the nozzle very satisfactorily; but it was found that with any but open charges of easy smelting ores accretions were liable to form against the sides of the furnace, building up to the level of the nozzle, and so decreasing the diameter of the furnace to the actual distance between tuyeres and defeating the purpose of the projecting tuyere nozzles. In addition, the accretions formed offered an advantageous surface for the accumulation of further masses of material, so the system has not been extended or come into general use. No tuyeres are introduced from either the front or the back of the furnace. By placing them sufficiently near the ends on the sides, ample blast penetration is provided and there is nothing in front to be in the way of tapping the slag. The number of tuyeres in the furnace will, of course, vary with the length. Usually one is placed on each side for each 20 inches in length. The opening is circular and varies from 3 to 4 inches in diameter.

79. Lead Tap.—Two methods of tapping the lead are possible: First, intermittently from the bottom of the crucible; second, either continuously or intermittently by means of an inverted siphon built into the crucible wall, as shown at *i*, Fig. 7. The latter is known as the **Arents siphon tap** and is the one in most general use. By it the lead may flow continuously if desired, always drawing from the bottom of the crucible and without the necessity for stopping the blast or any other disadvantages that must accompany the intermittent tapping of the metal. There is one case, however, in which the Arents tap cannot be used successfully, and that is where the charge carries a considerable amount of copper. It has already been stated that copper is liable to separate from the lead in the crucible, forming a mushy mass that soon causes the crucible to freeze up, since it cannot be replaced by hot lead from above. In such a case intermittent tapping from the bottom

of the crucible has been worked very successfully without cessation of blast, thus avoiding the difficulties usually occasioned thereby. It is, however, still open to the objection that by the removal of the molten lead from the crucible it much increases the chances that lumps of sintered ore, slag, fuel, etc. may find a lodging place upon the bottom thus left exposed and form a beginning of the much dreaded hearth accretions.

BLAST-FURNACE WORKING

80. Most Favorable Conditions.—The ideal conditions never actually occur in practice; even if no injurious elements are present, the gangue does not naturally form a good slag without further additions, and sulphur, at least, is almost invariably a constituent. It will, therefore, be well to consider next the running of the blast furnace on straight, easy, smelting charges, such as might occur in practical work.

81. Purchasing Ores for Mixtures.—Since the ores from different localities differ so widely, both in the desired mineral contained and in the gangue with which it is associated, it is possible, if the purchasing be rightly conducted, to provide for an ore mixture in which the different ingredients tend to offset one another. For instance, if the ore buyer has secured a lot of silicious ore from one district, it should be his aim to obtain a corresponding amount of limestone or iron-bearing ore from some other district, and in this manner try to neutralize the acid of the silicious ore. Again, as far as possible, combinations of sulphide and oxidized ores should be effected in purchasing; and in some cases ores containing deleterious ingredients to an extent that would render it impossible to smelt them alone may be "diluted," so to speak, with ore free from such ingredients to a point where smelting becomes not merely practicable, but also profitable—a distinction that is not always drawn with sufficient care. Possibly the clearest idea of the different steps involved may be gained by

following the ore in its course through the smelting works from the time it is received.

82. Basis of Ore Purchases.—Since it is impossible to keep separate the various lots of ore treated, custom smelting is, to all intents and purposes, an impossibility. The ores are, therefore, purchased outright by ore buyers. Since a number of factors enter into the relative values of different ores, it is desirable that a clear understanding should be had of the basis on which calculations are made, and this can best be had by taking up separately the various ingredients of the ores on the presence or absence of which the price depends.

83. Lead.—A charge must contain a certain percentage of lead in order to run at all; from 6 to 7 per cent. is a minimum that requires careful work to smelt. Therefore, less than 5 per cent. of lead in an ore is not paid for. If above that limit, the pay is so much per unit, based on market rates. A unit is 1 per cent. of a short ton, or 20 pounds.

84. Silver.—In purchasing ores containing silver, a deduction of 5 per cent. is made from the assay value to compensate for loss. The ore is settled for on a basis of 95 per cent. of its silver contents, as determined by fire assay.

85. Gold is paid for at the rate of $19 per troy ounce, if in excess of .05 ounce per ton. No deduction from assay value is made, the loss being covered by the price paid per ounce.

86. Base Metals and Metalloids.—**Copper** is not desirable, but must be paid for if over 2 per cent. fire assay. (Fire assay = wet assay − 1½ per cent.)

Should the percentage of **sulphur** be over 5 per cent., a charge is made for roasting. This charge varies, but is about $2 per ton of ore.

To determine the quantity of **silica** that an ore should contain, the percentages of iron and manganese are added,

and if the percentage of silica exceeds this sum, a charge of 10 cents per unit of excess is made.

Iron and **manganese** are added, and if the sum of their percentages exceeds that of silica SiO_2 present, the payment for such ore is made at the rate of 10 cents per unit of excess. It will be noted that the charge for silica SiO_2 or ferrous oxide FeO is based on the necessity of providing a flux for silica, if none is already present.

Lime or **magnesia** is paid for at varying rates; for instance, good limestone near a smelter will cost less than if obtained at some distance.

Zinc, when in excess of a fixed figure, which varies at different smelters, but which is in the neighborhood of 10 per cent., is charged against the ore seller at the rate of 50 cents per unit.

The presence or absence of **arsenic** and **antimony** also becomes a factor to an extent based on ore supply.

87. Percentage of Recovery.—As a matter of fact, the results of actual smelting operations are somewhat better than those allowed for in the foregoing scale; the recovery of lead and silver is closer, and gold is worth $20.67 an ounce instead of $19. The recovery of gold is so perfect that sometimes more is produced than is shown by the books to have gone into the furnace. On an average, the output of these metals is nearly 100 per cent. Therefore, after charging from $4 to $12 per ton for smelting, as a specific item, the poor but honest smelter is sometimes able to shade prices a little.

88. Separating Ores.—The ores that come to the works are divided into two main classes—those that require roasting and those that do not. These are separated at the time of their receipt, and are usually taken to the proper one of the two receiving houses, which are entirely separate and distinct from each other. Those that are not to be roasted require no crushing, so far as their subsequent treatment is concerned, but on the contrary it is most desirable to keep

them in lump form. They are, therefore, usually sampled by fractional selection in the process of unloading the car and discharged directly into the ore bins. The exception to this rule would occur in cases where the ore was very rich and more accurate sampling was desired. In such instances the entire lot would be crushed and cut down by hand.

All ores that are to be roasted must be crushed, consequently it saves handling to discharge them so that they will pass directly from the cars into the crushers. As the ores leave the crushers they are sampled by hand or by mechanical means, or possibly by a combination of both methods.

These two classes of ores are spoken of as **sulphide** and **oxidized ores** and will be so designated.

89. Ore Bedding.—Both classes of ore after sampling are made up into the mixture which accomplishes as nearly as possible the purposes discussed. The sulphide ores will

FIG. 19

be so combined that the galena ores will be mixed with those carrying large amounts of pyrites, and the oxidized ores so that basic vein material may be combined with acid. This

is accomplished by arranging the location of the different ores as they are unloaded from the cars. Each ore as received is spread out in a thin horizontal layer in a large bin, Fig. 19, covering the whole area as uniformly as possible. When the next ore for this bin is received, it is spread on the top of the ore just placed and so on until the bin is full. Due care, of course, must be taken to provide for the proper arrangement with reference to composition, as indicated above. When the ore from the bin is to be used, a door is opened at the side, as shown in Fig. 20, and the ore

Fig. 20

removed in such a way as to draw uniformly from all the horizontal layers that have been formed in the process of bedding. As the ore is shoveled from the floor of the bin, the different layers fall into the space thus left vacant in a fairly representative mixture of the different components, and the object aimed at, i. e., the production of a uniform mixture and one that will require as little addition of fluxes as possible, is attained. From the bins the ore goes either to the roasting furnaces or to the blast furnaces, as its character may require.

Fig. 21 shows an ore bed and the method of attacking it from its bottom. The different layers of ore are distinctly

FIG 21

shown by the horizontal bedding planes, and it can be seen that each shovelful will contain a portion of the various beds.

90. Making Up the Charge.—The iron ore and limestone are unloaded from the cars into the bins or in piles convenient to the blast-furnace charging floor. The man to whom is assigned the duty of making up the charges is kept supplied with all the different components, which are placed in separate piles around the scales. The scales are frequently especially designed for such purposes, being enclosed in a locked case, a separate beam being provided to indicate the weight of each component. In such a case, all that is to be done is to liberate the first beam and add the first ingredient until the corresponding indicator *a*, Fig. 22, shows that the weight apportioned to its beam has been reached; then to liberate the next one and add the next

component to the charge until its amount has been secured, and so on. The weight *b* represented by each beam is adjusted by some one in authority, so that the man who makes up the charge need not know the weight of a single

Fig. 22

component. The different ores and fluxes are usually mixed in the same ore buggy and run directly to the charging door of the blast furnace when the full amount has been weighed out. The coke is weighed separately, so that it may be charged in a distinct layer.

The lever *c* is drawn down and placed under notch *d*, to throw any given beam into action. If two or more levers are thrown down together, the scales will weigh the sum of the weights set on the beams corresponding to those levers.

91. Charging.—As a rule, the ore and fluxes are dumped into one pile, the coke into another, and the slag that is to be resmelted into a third. Sometimes ore and fluxes are kept separate. In charging, it is aimed to distribute the components of the charge in as uniformly horizontal layers as possible. The system of column charging is rarely attempted. The order in which the different ingredients are charged is more or less arbitrary. It is sometimes thought that a delay in the formation of the slag can be brought about by a separation of the unlike components, and in this case the charging is done with such a purpose in mind. The coke is always kept in a separate and distinct layer. Again, it is thought by some that the fuel may be so charged as to bring a larger proportion into any portion of the furnace that may appear to be somewhat chilled, so that when burned it may be at the chilled region; but it hardly seems that any real good can be accomplished in this way, since the materials must mix and lose their relative positions before they reach a point where combustion takes place. This is especially true in the cases where the formation of accretions has taken place in the furnace—the very point that it is desired to correct by the arrangement of the fuel charge. The material charged should settle evenly without any sudden drops, and the furnace should be kept filled nearly to the feeding door, unless for some reason it is desired to allow the charge to settle. It should be fairly cool at the top and no signs of flame or fire should appear.

92. Action in the Furnace.—The action as the charge settles into the lower regions of the furnace is rather uncertain. No one has ever been able to see it and guesses based on circumstantial evidence are the best that any one can offer. Probably, however, the following may fairly represent them.

The results produced by the blast furnace are brought about by the combustion of carbon above the tuyeres. This acts both as a producer of heat, which is necessary to most of the reactions taking place, and as a deoxidizer or

reducing agent. Even when partially oxidized, that is, as carbon monoxide, it acts in this latter capacity. The actual combustion of the fuel containing the carbon takes place at or slightly above the tuyere level. When the air is blown in through the tuyeres, the oxygen contained in it probably completely consumes the glowing fuel that it first meets, forming carbon dioxide. As this passes upwards, however, it at once comes into contact with further amounts of incandescent carbon and forms $CO_2 + C = 2CO$; this carbon monoxide is doubtless the agent that accomplishes all but the most difficult reductions.

With this explanation in mind, the next step is to trace the materials charged in at the top in their progress through the furnace. The materials are ores, fluxes, and slag (which in the present case may be considered as playing a part purely physical) and the fuel itself. The substances to be considered are lead, present as oxide, carbonate, sulphate, sulphide, arsenate, antimonate and silicate, silver chloride and sulphide, ferric oxide, calcium carbonate, silica, and silicates. Other materials present are either substances that act like types already included, as magnesium carbonate, which acts similar to calcium carbonate, or that occur in such small amounts that their total effect can be neglected.

In the upper part of the furnace the only action is that due to heat; as, for example, the decomposition of the carbonates $PbCO_3 + \text{Heat} = PbO + CO_2$. At a higher temperature, $CaCO_3 + \text{Heat} = CaO + CO_2$. Reduction by carbon monoxide of easily reducible oxides in the form of fine material or porous lumps next takes place. It is difficult to see how any other action can go on until a condition of incipient fusion of the principal lead compounds is reached at a temperature of about 1,000° C. This practically marks the upper limit of the zone of active chemical effect. Here lead sulphide acting on lead oxide and lead sulphate produces metallic lead; carbon monoxide reduces lead oxide to metallic lead, lead sulphate to lead sulphide, and lead arsenate and antimonate to arsenide and antimonide, respectively. Ferric oxide is reduced by the same agent to ferrous oxide.

Lime acts on lead silicate, liberating lead oxide, which in turn is reduced to metallic lead. Silver chloride and sulphide are reduced to silver by the lead already formed. Finally the lime and ferrous oxide combine with the silica and silicates to produce the slag. A certain amount of ferrous oxide is reduced by incandescent carbon to the metallic state and then acts upon a portion of the sulphide and arsenide of lead present in accordance with the following formula:

$$PbS + Fe = Pb + FeS$$

The same action takes place with the arsenide, resulting in the formation of matte and the decomposition of all but the very small part of the lead contents of the charge that is found in the matte. If the proper proportions of fuel and blast have been used, all the lead should be reduced and that found in the slag should be only finely divided particles carried mechanically.

CALCULATING FURNACE CHARGES

93. Calculating the Charge.—Although it has been planned as far as possible to arrange the different ores in such a manner that the components of the gangue shall be so matched as to approach as nearly as possible to the slag that is to be made, in practice any really close approximation is not usually possible. In this country silicious ores predominate, and in almost every instance it will be found necessary to add some basic material as a flux. The usual sources of such material are iron ore and limestone. At times, iron that carries appreciable values in gold may be obtained as a flux.

In most smelting centers iron ore is the more costly, so that the aim will be to make up a slag containing as much lime and as little iron as may be consistent with good running. Also, since both materials must be bought, it will be seen that it is desirable to make the silica as large a component of the slag as possible. By knowing the composition

of the ore that is coming from the roasting furnace and that of the oxidized ore from the bedding bins, it will be possible to calculate what proportions of each and how much additional fluxing material of each sort will be needed to make up a charge that will result in the formation of the desired slag when melted in the blast furnace. This arrangement of materials having been made, the man that makes up the charge for each furnace is informed that he is to take so many pounds of ore from such a roasting furnace, so many pounds of ore from one bin, so many pounds of ore from another, so much limestone, and so much iron ore, in this manner making up a charge that usually amounts to 1,000 pounds.

94. To the beginner the calculation of blast-furnace charges seems a tremendous task, but a little experience soon robs it of its terrors. The furnaceman rarely calculates an entire charge, as he has learned by practice what approximate weights of each material he requires, and the simple operation of footing up the silica, lime, and iron contained in each component shows him whether or not his guess has been correct. One or two modifications will usually give him the slag he is after. A practical example will show the method, and for the sake of simplicity only whole percentages will be used, since that will in no way affect the method.

The main slag for the lead smelter is the singulosilicate slag with oxygen ratio of bases to silica as 1 : 1; for example, $2RO + SiO_2$ or $2R_2O_3 + 3SiO_2$. Another slag sometimes made is termed sesquisilicate with the oxygen ratio of bases to silica as 2 : 3; for example, $4RO + 3SiO_2$ or $4R_2O_3 + 9SiO_2$. The latter slag is not as fusible as the singulosilicate and, hence, is not used except when a high temperature is desirable. According to the ratio of FeO to CaO, the slag used for an example to be made is termed $1\frac{1}{2}$: 1 slag and is to contain $24CaO$, $30SiO_2$, and $36FeO$. The sum of the three ingredients foots up to 90 per cent., it being customary to leave 10 per cent. for other ingredients

of the ore, like old slag and substances that cannot be brought under the head of ferrous oxide and calcium oxide, like manganese oxide, baryta, and magnesia oxides. The conditions that govern the charge are 10 per cent. of old slag, 16 per cent. of fuel, and 1,000 pounds of all ingredients to the charge.

95. Assume that the composition of the ore and fluxes is according to Table I.

TABLE I

	Ore Mixture	Fluxes		Coke Ash $12\frac{1}{2}$% Total Coke Wt.
		Iron Ore	Limestone	
Pb	25.0%	..	..	..
Ag ounces per ton	60.0	5	..	..
Cu	3.0%	..	..	..
SiO_2	25.0%	3%	2%	40.0%
FeO	10.0%	68%	4%	20.0%
MnO	5.0%	2%	..	..
CaO	2.2%	2%	36%	6.5%
MgO	2.0%	..	10%	2.5%
ZnO	2.0%	..	..	..
Al_2O_3	2.0%	..	..	25.0%
S	5.0%	..	..	..
As	1.0%	..	..	..

96. In the direct calculation, only the silica, lime, and iron are considered. Those that act similar to any one of these are calculated and expressed in their chemical equivalents. For example, the ore mixture contains 2.2 per cent. of CaO; it also contains 2 per cent. of MgO, which acts similarly in the slag. But the atomic weight of Mg is 24, while that of Ca is 40; that is, 24 pounds of Mg is chemically equivalent to 40 pounds of Ca, and as the atomic weight of O is 16, the

following proportions will be the chemical equivalent of MgO in terms of CaO.

$$MgO : CaO = (24 + 16) : (40 + 16) = 40 : 56;$$

and since there is 2 per cent. of MgO,

$$40 : 56 = 2 : 2.8 \text{ per cent. of } CaO$$

This added to the 2.2 per cent. of CaO present gives 5 per cent. of CaO or its equivalent in the ore mixture. Next taking the limestone, it is seen that 10 per cent. of it is MgO, therefore $40 : 56 = 10 : 14$, so that in the limestone there is $36 + 14 = 50$ per cent. of CaO or its equivalent. By a parallel course of reasoning, it will be seen that the coke ash contains the equivalent of

$$6.5 \text{ per cent.} + (\tfrac{56}{40} \times 2.5 \text{ per cent.}) = 10 \text{ per cent. of } CaO$$

97. Manganese oxide MnO acts almost like ferrous oxide FeO in the slag, and as the atomic weights differ so little, MnO may be considered directly equivalent to FeO weight for weight. The ore mixture will, under such terms, contain 10 per cent. + 5 per cent. = 15 per cent. of FeO and the iron ore 68 per cent. + 2 per cent. = 70 per cent. of FeO.

The aluminum oxide Al_2O_3 and the zinc oxide ZnO may be left out of the calculation for the present and only the essential slag-forming elements noted.

These may be put in the following simplified form :

TABLE II

Slag Element	Ore Mixture. Per Cent.	Fluxes		Coke Ash. Per Cent.
		Iron Ore. Per Cent.	Limestone. Per Cent.	
SiO_2.......	25	3	2	40
FeO.......	15	70	4	20
CaO.......	5	2	50	10

98. To proceed with the actual calculation, ascertain the fluxes necessary to flux the coke ash in a charge of 1,000 pounds. 1,000 × 16 per cent. = 160 pounds of coke, and 160 × 12.5 = 20 pounds of coke ash to be fluxed. Assume that this will combine with x pounds of limestone and y pounds of iron ore to produce the required slag. The two equations necessary to determine the unknown quantities are found in the double ratio contained in the slag required.

$$SiO_2 : FeO : CaO = 30 : 36 : 24.$$

That is, the total SiO_2 in the coke ash, iron ore, and limestone must bear the ratio of 30 : 36 to the total FeO and the ratio 30 : 24 to the total CaO in those materials. Putting it in the form of equations and obtaining the values for x and y from Art. **97**,

$$\frac{.40 \times 20 + .02\,x + .03\,y}{.20 \times 20 + .04\,x + .7\,y} = \frac{30}{36},$$

or $.40 \times 20 + .02\,x + .03\,y = \frac{5}{6}\,(.20 \times 20 + .04\,x + .7\,y)$;

then, $$48 + .12\,x + .18\,y = 20 + .20\,x + .35\,y.$$
$$3.32\,y = 28 - .08\,x.$$
$$y = 8.43 - .0024\,x.$$

$$\frac{.40 \times 20 + .02\,x + .03\,y}{.10 \times 20 + .5\,x + .02\,y} = \frac{30}{24},$$

or $.40 \times 20 + .02\,x + .03\,y = \frac{5}{4}\,(.10 \times 20 + .5\,x + .02\,y)$;

then, $$32 + .08\,x + .12\,y = 10 + 2.5\,x + .1\,y.$$
$$.02\,y = 2.42\,x - 22.$$
$$y = 121\,x - 1{,}100.$$
$$8.43 - .0024\,x = 121\,x - 1{,}100.$$
$$121.0024\,x = 1{,}108.43.$$
$$x = 9+ \text{ pounds of limestone.}$$
$$y = 8- \text{ pounds of iron ore.}$$

That is, when all the 20 pounds of coke ash is fused with 8 pounds of iron ore and 9 pounds of limestone, it will form a slag of the required composition, as may be ascertained by trial.

TABLE III

Slag Element	SiO_2 Pounds	FeO Pounds	CaO Pounds
20 pounds coke ash contain.	.4 × 20 = 8.00	.2 × 20 = 4.00	.1 × 20 = 2.00
8 pounds iron ore contain..	.03 × 8 = .24	.7 × 8 = 5.60	.02 × 8 = .16
9 pounds limestone contain.	.02 × 9 = .18	.04 × 9 = .36	.5 × 9 = 4.50
Total..................	8.42	9.96	6.66

The slag thus formed will contain its chief ingredients in the following ratio :

$$SiO_2 : FeO : CaO = 8.42 : 9.96 : 6.66.$$

In order to compare this ratio with the standard that is aimed at—namely,

$$SiO_2 : FeO : CaO = 30 : 36 : 24,$$

it is necessary to multiply through by the coefficient

$$\frac{30 + 36 + 24}{8.42 + 9.96 + 6.66} = \frac{90}{25.04} = 3.594.$$

Performing the operation,

$$\begin{aligned} SiO_2 : FeO : CaO &= 3.594\,(8.42 : 9.96 : 6.66) \\ &= 30.26 : 35.80 : 23.94, \end{aligned}$$

which is sufficiently close, considering the relatively small quantity in a charge of 1,000 pounds.

99. The necessary quantities of iron and limestone for combination with the gangue of the ore mixture are calculated in a manner similar to that of coke ash, with the difference that it is not yet known how much ore will enter a 1,000-pound charge. Assuming, therefore, for convenience, 100 pounds of ore and representing the limestone necessary for such a charge by x' and the ore by y', proceed as before to find the total amount of each substance in the same ratio as that fixed for slag.

In the form of equations,

$$\frac{.25 \times 100 + .02\,x' + .03\,y'}{.15 \times 100 + .04\,x' + .07\,y'} = \frac{30}{36} = \left(\frac{SiO_2}{FeO}\right). \qquad (1)$$

$$\frac{.25 \times 100 + .02\,x' + .03\,y'}{.05 \times 100 + .50\,x' + .02\,y'} = \frac{30}{24} = \left(\frac{SiO_2}{CaO}\right). \qquad (2)$$

Clearing (1) of fractions,

$$\frac{25 + .02\,x' + .03\,y'}{15 + .04\,x' + .7\,y'} = \frac{30}{36} = \frac{5}{6}.$$

$$6\,(25 + .02\,x' + .03\,y') = 5\,(15 + .04\,x' + .7\,y').$$
$$150 + .12\,x' + .18\,y' = 75 + .2\,x' + 3.5\,y'.$$
$$75 = .08\,x' + 3.32\,y'. \qquad (3)$$

Clearing (2) of fractions and finding value of y',

$$4\,(25 + .02\,x' + .03\,y') = 5\,(5 + .5\,x' + .02\,y').$$
$$100 + .08\,x' + .12\,y' = 25 + 2.5\,x' + .1\,y'.$$
$$75 = 2.42\,x' - .02\,y'.$$
$$y' = 121\,x' - 3{,}750. \qquad (4)$$

Substituting this value of y' in (3) and solving for x,

$$75 = 401.8\,x' - 12{,}450.$$
$$x' = 31.172.$$

Substituting the value of x' in (4),

$$y' = 3{,}771.812 - 3{,}750.$$
$$y' = 21.812.$$

Omitting figures after the first decimal place,

$x' = 31.1$ pounds of limestone for each 100 pounds of ore mixture.

$y' = 21.8$ pounds of iron ore for each 100 pounds of ore mixture.

TABLE IV

PROOF TABLE

Slag Element	SiO_2 Pounds	FeO Pounds	CaO Pounds
100 pounds ore mixture contain	$.25 \times 100 = 25.00$	$.15 \times 100 = 15.00$	$.05 \times 100 = 5.00$
31.1 pounds limestone contain	$.02 \times 31.1 = .62$	$.04 \times 31.1 = 1.24$	$.50 \times 31.1 = 15.55$
21.8 pounds limestone contain	$.03 \times 21.8 = .65$	$.70 \times 21.8 = 15.26$	$.02 \times 21.8 = .43$
Total	26.27	31.50	20.98

That is, the slag thus formed contains

$$SiO_2 : FeO : CaO = 26.27 : 31.5 : 20.98.$$

Comparing as before,

$$\frac{30 + 36 + 24}{26.27 + 31.5 + 20.98} = \frac{90}{78.75} = 1.143.$$

Multiplying through by this coefficient gives

$$SiO_2 : FeO : CaO = 1.143(26.27 : 31.5 : 20.98)$$
$$= 30.026 : 36.004 : 23.98.$$

100. The calculation has thus far resulted approximately in accordance with the conditions prescribed. This completes the consideration of the slag-making materials, but the ore mixture has in it elements that will reappear in the form of matte and speiss; these must also be taken into account.

There are present 3 per cent. of Cu and 5 per cent. of S, or in 100 pounds of ore mixture 3 pounds of copper and 5 pounds of sulphur. Sulphur has a greater affinity for copper than for iron, and copper will be present in the matte as copper sulphide Cu_2S; therefore, since atomic weight of copper is 63.4 and of sulphur 32, the proportion of S in the matte is found by

$$Cu_2 : S = 126.8 : 32 = 3 : .76 \text{ pound of } S \text{ as } Cu_2S$$

But in 100 pounds of ore mixture there were 5 pounds of sulphur; therefore, there will be $(5 - .76) = 4.24$ pounds of sulphur left, which must take up metallic iron from FeS. By a similar proportion, the atomic weight of iron being 56, $S : Fe = 32 : 56 = 4.24 : 7.42$ pounds of iron necessary to combine with 4.24 pounds of sulphur remaining.

101. In 100 pounds of the mixture there will be 1 pound of arsenic, according to analysis. This must be provided with sufficient iron to form Fe_5As, the desired speiss. The atomic weight of arsenic is 75; hence, by proportion $As : Fe_5 = 75 : 280 = 1 : 3.73$ pounds of metallic iron necessary to unite with 1 pound of arsenic to form speiss. To form matte and speiss will require $7.42 + 3.73 = 11.15$ pounds of metallic iron for each 100 pounds of the ore mixture. This metallic substance is to be obtained from a farther addition of iron ore to the charge.

102. Since the iron ore contains silica SiO_2, due allowance must be made for it. In this case there is 3 per cent. of silica present, which, according to the slag ratio $SiO_2 : FeO = 30 : 36$, will require 3.6 per cent. of FeO to combine with it to form slag. Atomic weight $SiO_2 = 60 : FeO = 72 = 30 : 3.6$. There is available, therefore, $70 - 3.6 = 66.4$ per cent. of FeO for the purposes in hand. The quantity of metallic iron to which this is equivalent is found by the following proportion:

$FeO : Fe = 72 : 56 = 66.4 : 51.6$ per cent. of metallic iron available.

For 100 pounds of ore mixture, 11.15 pounds of metallic iron were required according to Art. **101**, which is the amount available in $\frac{11.15}{.516} = 21.6$ pounds of iron ore.

To sum up, the amount of limestone and iron ore that each 100 pounds of the ore mixture will require may be found in Table V.

TABLE V

	For Slag. Pounds	For Matte and Speiss. Pounds	Total. Pounds
Limestone	31.1		31.1
Iron ore	21.8	21.6	43.4
Total fluxes	52.9	21.6	74.5

The amount of CaO required by the SiO_2 in this amount of ore to complete its slagging is .52 pound, while there is .43 pound already present in the ore; the difference .09 pound might be supplied by adding a proportionate quantity of limestone, but the amount is so small it can be neglected.

103. To proceed with the actual make-up of the charge. As originally stated, the charge was to be 1,000 pounds and was to contain 10 per cent. of old slag and 16 per cent. of fuel. Only the ash of the fuel, however, which amounts to 12½ per cent. of the total weight, is figured as entering the charge. The fixed quantities in the charge are, therefore, old slag, 100 pounds; ash, 20 pounds. The fluxes for ash (obtained by calculation) are iron ore, 8 pounds; limestone, 9 pounds. The amount that is to be made up of ore mixture and required fluxes is 863 pounds, making a total of 1,000 pounds.

It was found that the amount of fluxes required by 100 pounds of ore mixture was 74.5 pounds; therefore,

$$\text{Ore in 1,000-pound charge} = 100 \times \frac{863}{174.5} = 494.5 \text{ pounds.}$$

$$\text{Fluxes for ore} = 74.5 \times \frac{863}{174.5} = 368.5 \text{ pounds,}$$

of which there were 153.85 pounds of limestone and 214.65 pounds of iron ore.

Omitting fractions and taking the total quantity of iron ore and limestone regardless of purpose, the final make-up

of the charge is: Ore mixture, 495 pounds; iron ore, 222 pounds; limestone, 163 pounds; coke ash, 20 pounds; old slag, 100 pounds; making a total of 1,000 pounds.

104. When the result is placed in tabular form, the same elements from the various constituents being brought together, the desired deductions can be more readily made. In Table VI, the 222 pounds of iron ore are for the purposes of forming slag, as FeO, and forming matte and speiss, as Fe. For the latter purpose, 101.4 pounds of iron ore yield the required amount, since it contains 54.4 per cent. of Fe = 70 per cent. of FeO; this leaves 120.6 pounds to supply FeO for slag, the amount contained therein being sufficient to meet the requirements of all SiO_2 present in the charge.

TABLE VI

Substances in the Charge	Ore Mixture		Iron Ore		Limestone		Coke Ash		Old Slag		Total
Pounds	495		222		163		20		100		1,000
	Per Cent.	Pounds	Per Cent.	Pounds	Per Cent.	Pounds	Per Cent.	Pounds	Per Cent.	Pounds	Pounds
Silica SiO_2	25	123.75	3.0	6.66	2	3.26	40	8.00	30	30	171.67
FeO	15	74.25	70.0	84.43	4	6.52	20	4.00	36	36	205.20
Fe			54.4	55.20							55.20
CaO	5	24.75	2.0	4.44	50	81.50	10	2.00	24	24	136.69
Al_2O_3	2	9.90					25	5.00			14.90
ZnO	2	9.90									9.90
Ag. oz. (*b*).....	60	14.85	5.0	.55							15.40
Pb (*a*).........	25	123.75									123.75
As (*c*).........	1	4.95									4.95
Cu (*e*).........	3	14.85									14.85
S....	5	24.75									24.75

105. Taking the chief ingredients of the slag in pounds as obtained from Table VI, it is seen that the slag resulting from such a charge will have a ratio

$$CaO : SiO_2 : FeO = 136.69 : 171.67 : 205.20.$$

Multiplying through by the coefficient

$$\frac{24 + 30 + 36}{136.69 + 171.67 + 205.20} = .17525$$

to reduce to comparable terms, as in former cases, gives the ratio.

By multiplying the weights of ZnO and Al_2O_3 in the charge by the same factor or coefficient ($.17525 \times 9.9 = 1.73$ parts ZnO : $.17525 \times 14.9 = 2.61$ parts Al_2O_3), the relative amounts of each in the slag may be found.

106. The following additional information may be gained from Table VI:

(*a*) 1,000 pounds of charge contains 123.75 pounds, or 12.375 per cent. of lead.

(*b*) The base bullion produced should contain 15.4 ounces of silver for each 123.75 pounds of lead by the proportion $123.75 : 2{,}000 = 15.4 : 249$ ounces of silver are contained in 2,000 pounds of base bullion.

(*c*) The 4.95 pounds of arsenic in the ore mixture will unite with the iron in the proportion $75 : 280 = 4.95 : 18.48$ to form speiss; the weight of the speiss formed from 100 pounds of charge will, therefore, be $4.95 + 18.48 = 23.43$ pounds of speiss.

(*d*) The total quantity of slag from 1,000 pounds of charge is $171.67 + 205.20 + 136.69 + 14.90 + 9.90 = 538.36$ pounds.

(*e*) The remainder of the iron is $55.20 - 18.48 = 36.72$ pounds, which is the amount that will unite with the 14.85 pounds of copper and the 24.75 pounds of sulphur to form matte. The weight of the matte in the 1,000 pounds of charge will, therefore, be $36.72 + 14.85 + 24.75 = 76.32$ pounds.

(*f*) The above calculations give theoretical results, which are only approximately correct since there will be elimination of sulphur and arsenic by heat that will pass off with furnace gases. This will change the results somewhat, so their practical effect cannot be predicted on any theoretical basis.

LEAD SMELTING AND REFINING

(PART 2)

BLAST-FURNACE OPERATIONS

1. Blowing In.—Starting operations in a lead blast furnace is technically called **blowing in.** The first step consists in thoroughly drying and warming the masonry of the crucible and hearth by maintaining a cord-wood fire in it from 24 to 36 hours, the ashes being removed when necessary to keep the fire in good condition and in effective contact with the masonry. This should accomplish the thorough drying and warming of the crucible walls, but a higher heat is necessary before the actual charging can take place, otherwise the molten lead will be liable to freeze in the crucible and bring operations to a sudden and undesired termination. To gain this higher heating, a fire of charcoal or coke must be used and a blast introduced by means of a temporary iron pipe through the slag or siphon tap; after this has been continued for 6 or 8 hours, all ashes should be thoroughly removed and the blowing in proper may then begin.

The methods for accomplishing this depend on whether or not suitable charcoal can be had for the purpose. If it can be obtained, one of two methods may be followed: In the first, a fire is started by means of glowing charcoal upon the bottom of the hearth; more charcoal is added and a blast introduced, as before, by means of a temporary iron pipe, until the crucible is full of burning fuel. The breast of the furnace should then be put in place and another layer of charcoal charged from the top. Upon this come successive

layers of coke to about the top of the water-jackets, with enough bars of metallic lead to fill the crucible when they are melted down. Above this follow alternate layers of coke and slag, then coke, slag, and a small amount of ore with proper fluxes to make an easily fusible slag. By this time the furnace will be nearly full and the blast through the tuyeres should be started. The pressure should be low at first, since too rapid combustion of the charcoal will cause the lead to fuse and run down before the coke has been thoroughly ignited.

The aim should be to confine the combustion to the region immediately in front of the tuyeres as nearly as possible. In this way the charcoal will be thoroughly burned by the time the coke is well lighted, and when the lead comes down the fire will be sufficient to keep it hot and the danger of the crucible freezing will be avoided.

As the lead descends, the ashes of charcoal and coke float upon it; these are taken up by the slag, which begins to fuse soon afterwards. In the meantime, the material in the furnace having settled, additional charges, first of half slag and half ore with the necessary fuel and fluxes, and finally of easy-smelting charges of ore, fluxes, and fuel alone are introduced through the feed-door, when the furnace may be considered in operation.

2. A variation of this method is to fill the furnace entirely before any fire is kindled. In this method the charcoal is charged until it reaches perhaps a foot above the tuyere level, then follows coke for a depth of 2 or 3 feet, then bars of lead sufficient to fill the crucible as before, and finally, in due order, charges of slag and ore and ore alone. When the furnace is filled, the charcoal is kindled from the tuyeres and the blast started gently. The effect of this method is to leave the charcoal in the part of the furnace below the tuyere level unconsumed during the earlier stages of the operation. When the lead is fused, it comes down and floats the charcoal, gradually raising it to the level of the tuyeres, where it is consumed.

3. It is usually impossible to utilize coke for blowing in the furnace without previously filling the crucible with molten lead. The ash of coke is refractory and difficult of disposal, hence would accumulate on the hearth bottom and cause subsequent hearth accretions. Therefore, in order to blow in a furnace where only coke is available, the breast of the furnace is left open and a coke fire started in the crucible; bars of lead and fresh supplies of coke are introduced through the breast, air being supplied by means of a temporary iron pipe. This action is maintained until the crucible is full of molten lead, when all ashes should be raked from the surface, fresh kindling and coke introduced, and the breast put in. Charging from above is then begun, after which the operation is similar to that described. A slight crust may form over the surface of the lead, but this can usually be broken up by introducing a bar through the tap hole.

4. Blowing Out.—When it is desired to discontinue the operation of the furnace, ore charging is stopped, coke and slag only being added; then all charging ceases and the material in the furnace is allowed to settle until heavy smoke appears. One of two plans may then be followed: The connection with the flues may be closed and the blast continued until the material last charged has settled to the top of the water-jackets, the furnace gases being carried off by means of the stack. Then the blast is shut off and the breast jackets removed. The contents of the furnace are next raked out as rapidly as possible, while the lead is dipped from the crucible. In following the other plan, the blast is shut off entirely and all the material remaining in the furnace removed through the openings in the front left by the removal of the breast jackets.

5. Irregular Working.—Under certain circumstances, accretions are liable to form on the walls of the blast furnace, by the volatilization of material in the lower portion, which condenses upon the walls above. These grow to such proportions that they interfere seriously with the working of

the furnace, in some cases so contracting the cross-section at points as to cause practically a cessation of smelting operations in the region thus affected. In order to remove them, it is necessary to let the charge sink until they may be removed from the walls by means of steel bars driven between them and the walls. The accretions may be allowed to fall upon a bed of coke placed for the purpose upon the top of the charge. If the quantity should be excessive, it may be removed through an opening made in the brickwork just above the water-jackets.

6. Hearth accretions are frequently more difficult to dispose of. If the accretion takes the form of a crust across the top of the crucible, it may be possible to break it up by introducing a bar through the tap hole and driving holes through it; then by adding fresh lead above, the hot lead and slag coming down gradually take up the frozen material. If the accretions are building up from the bottom of the hearth, it is almost impossible to remove them. In such cases the furnace is run as long as practicable and must then be blown out and repaired.

7. Removing Defective Jackets.—It is possible to take out a defective jacket and replace it with a new one in the following way: The amount of water flowing through the jacket should be increased to a maximum for some little time, in order to cause the formation of a wall of chilled slag next to it in the interior of the furnace. Then the water supply should be shut off, and by working quickly the jacket may be taken out and a new one put in place before the wall of chilled slag breaks through to any serious extent.

8. Tapping.—Slag, matte, and lead, all in a molten condition, have now collected at the bottom of the furnace in the crucible. The relative positions of the different materials due to the difference in specific gravity will probably be in the order indicated above. Since the lead is so much greater in its specific gravity than either of the other two materials, it settles out fairly completely. The slag and matte, however, do not differ so widely and are more or less

mixed, therefore no attempt is usually made to separate them before tapping; both are drawn out together and allowed to separate in some form of external receptacle The tap hole for matte and slag is an opening in the tapping jacket, circular in cross-section, and somewhat larger at the inside than at the outside; in other words, it forms a truncated cone with the smaller base about 2.5 inches in diameter, while the larger base is probably twice that size. It is placed about 8 inches below the level of the tuyeres, so that if tapping should at any time be delayed beyond the regular period, the slag might rise to that extent without flowing into the tuyere ports. When tapping, the slag notch is allowed to remain open until the level of the slag is so reduced that the blast begins to blow through it; it is then plugged at one stroke with a cone of plastic fireclay.

9. The clay is kneaded into shape by the tapper and then affixed to a steel rod, which terminates in a flat disk about 3 inches in diameter; when this disk has been dipped in water, the clay will adhere to it without difficulty. When the tap hole has been thus closed, the tapper clears the iron slag spout that conveys the slag over the masonry of the crucible wall, applies a thin wash of clay and water to keep slag from adhering, and puts things in order for the next tapping. The time that elapses before this occurs varies with the rate at which the furnace is making slag; possibly 3 minutes would be a fair average. By this time the clay in the tap hole has become baked pretty hard; but if the slag within has not frozen, it should be possible to penetrate to the molten slag by a few well-directed blows with a pointed steel bar, after first removing the loose clay from the exterior. The accumulated slag then begins to flow and assists in clearing the tap hole. If it comes slowly, and thus indicates the presence of obstructions, a steel rod is thrust directly through to the liquid slag within and worked back and forth until the slag flows freely. The tap hole is allowed to remain open, as before, until the blast begins to blow through it, when it is once more closed. The time it remains

open varies, of course, with the condition of the furnace; but in general it is open about as long as it has remained closed just previously.

The molten lead may either overflow continuously from the lead well into an entirely independent receptacle or it may be retained in the lead well by a dam of fireclay, to be tapped at intervals. The former practice is the better, however, since it keeps the molten lead in the receptacle at a uniform height and does not interfere with or change the level of the slag and the matte.

10. Slag Removal.—The slag is ordinarily removed from the blast furnace in specially constructed pots or slag cars. Its ultimate disposal depends on circumstances connected with the location of the furnace. A certain amount is always retained to be resmelted; aside from this, it may be utilized as foundations for new furnaces or buildings about the works by being poured molten into the excavations prepared; hollows may be filled with it, or it may be granulated or chilled in small lumps, to be used for railroad ballast.

FIG. 1

Granulating proper is accomplished by allowing the slag to flow in a thin stream into a much larger stream of flowing water. The danger from explosions in granulating slag in

this way is much less than in similarly granulating matte. Water and chilled slag run together into a car from which the water drains, leaving the slag to be removed.

A successful piece of apparatus for chilling slag without granulating it is in use at the Omaha smelters. The molten slag is poured into a ring-shaped iron trough very flat and with the bottom in contact with water to cool it. This trough is revolved about the center of the ring and the slag spreading out to a thickness of about $\frac{1}{4}$ inch immediately chills, breaking away from the iron and cracking into small pieces. At a point nearly opposite that at which the slag is poured on, a scraper is placed diagonally to the motion of the trough, so that the chilled slag is removed and conveyed through a chute into railroad cars, to be used for track ballast.

In Fig. 1 is shown a slag pot to be moved about by

FIG. 2

hand. This character of pot is also used as a matte and slag pot; the matte after cooling is broken off, as shown at *a*.

In Fig. 2 is shown a slag car with two bell-shaped pots. These are so arranged that they can be dumped one at a time on opposite sides or on the same side of the car frame.

FIG. 3

In Figs. 3 and 4 are shown two slag pots being dumped over the bank.

SLAGS

11. Composition of Slags.—While the subject of slag composition is of the utmost importance, definite information concerning it is rather deficient. To consider the general composition of slags, it must be borne in mind that the gangue of the great majority of smelting ores in this country is silicious, i. e., it contains either quartz, which is pure silica, or minerals running so high in silica that that element predominates all the other materials present. Silica in itself is infusible even at much higher temperatures than those attained in a lead blast furnace; and since it is to be separated from the lead by bringing both to a molten condition, it must consequently be combined with something that will render it fusible. It will be well worth while to consider rather carefully the nature and purpose of the compounds into which it may enter.

12. Silica SiO_2 is the characteristic component of a series of acids, just as the oxides of phosphorus go to make up

another, though different, series of acids. It will, therefore, combine with various bases to form salts known as silicates; furthermore, it will combine with these bases in widely varying proportions, not only in proportions that can be indicated by a simple chemical symbol, as, for example, $CaO \cdot SiO_2$, but in proportions that would be very complex if represented by numbers. In such cases, however, it seems probable that

FIG. 4

compounds are formed that represent a certain series of combinations, in all of which the ratio between the amount of base and acid present is definite and comparatively simple, and that these are soluble when in a state of fusion. Such has been assumed to be the case, and the various members of the series have been named according to a system based on this ratio, using the symbol $\ddot{R}$ as explained for such elements

as calcium, magnesium, and ferrous iron. The silicates of the corresponding bases would be named as follows:

$4\ddot{R}O \cdot SiO_2 =$ Subsilicate.
$2\ddot{R}O \cdot SiO_2 =$ Monosilicate.
$\ddot{R}O \cdot SiO_2 =$ Bisilicate.
$4\ddot{R}O \cdot 3SiO_2 =$ Sesquisilicate (Sesqui = $1\frac{1}{2}$).

These names are derived from the ratio of atoms of oxygen associated with Si to atoms of oxygen associated with $\ddot{R}$, as will be seen on comparison.

Subsilicate $= (2 : 4) = \frac{1}{2} : 1.$
Monosilicate $= (2 : 2) = 1 : 1.$
Bisilicate $= 2 : 1.$
Sesquisilicate $= (6 : 4) = 1\frac{1}{2} : 1.$

13. Correspondingly, for such bases as have the same form as aluminum oxide Al_2O_3, the symbol $\dot{\ddot{R}}_2O_3$ would be used and the make up of the silicates would be as follows:

$4\dot{\ddot{R}}_2O_3 \cdot 3SiO_2 =$ Subsilicate; ratio, $6 : 12 = \frac{1}{2} : 1.$
$2\dot{\ddot{R}}_2O_3 \cdot 3SiO_2 =$ Monosilicate; ratio, $6 : 6 = 1 : 1.$
$\dot{\ddot{R}}_2O_3 \cdot 3SiO_2 =$ Bisilicate; ratio, $6 : 3 = 2 : 1.$
$4\dot{\ddot{R}}_2O_3 \cdot 9SiO_2 =$ Sesquisilicate; ratio, $18 : 12 = 1\frac{1}{2} : 1.$

14. Bases.—Combinations of silica and bases in which the ratio of silica to base cannot be thus simply expressed are thought to be probably either mixtures of the simple forms, or possibly the relation may be that which exists in a solution. Be this as it may, the essential point is that the fusibility in general decreases with an increase of silica, and naturally the fluidity of the hot slag decreases correspondingly. The fusibility of the slag, however, depends not merely on the ratio of silica to base in it, but also on the bases themselves. In the first place, the silicates of some bases are much more fusible than the exactly corresponding silicates of others; for example, the silicates of alumina are for the most part very difficultly fused, fireclay itself being one of them, while the corresponding *ferrous* silicates are comparatively readily fused.

NOTE.—The distinction between the *ferrous* and *ferric* forms should be carefully noted; the former are much more fusible than the latter, and in lead slags the iron is always assumed to be present in the ferrous form.

15. Silicates With One Base.—In the second place, the silicate containing but one base is, other things being equal and the proportion of base to acid remaining the same, less fusible than one containing two or more bases. With these fundamental principles in mind, the requirements of the special case in hand, i. e., lead smelting, should be carefully considered. These requirements briefly stated are as follows.

16. The temperature of the slag must not be so high as to cause volatilization of lead. This would result in losses of both lead and the precious metals carried over mechanically with the lead. The consumption of fuel would also be needlessly increased.

17. The formation temperature of the slag must be sufficiently high to prevent the slag forming before the lead compounds have had time to be completely converted into metallic lead. The effect of such a condition is that the complete fusion of the charge does not take place until it has descended nearly or quite to the tuyere, and, therefore, into the narrow part of the furnace where the heating effects of the fuel are concentrated. Strange as it may seem at first glance, the avoidance of a slag with an excessively low formation temperature results in an actual economy of fuel.

18. The slag that is formed should have such physical properties as to afford a ready and complete separation from matte and base bullion. Since this depends primarily on the difference in specific gravity, the aim should be to make a slag as low in specific gravity as may be possible without interfering with the other desirable properties. Again, at the temperature at which it is drawn from the furnace its viscosity should be so slight that it will not retain mechanically **shots** or **prills** of matte or metal, but will allow them to settle out rapidly and completely.

19. Quantity of Flux to be Added.—For economical reasons the amount of flux added should be as small as may be consistent with the properties previously enumerated. The gain or loss will appear in several different places, in the accounts of the company. In the first place, the fluxes themselves must all be either purchased or mined, so that a practical saving is effected when their use is cut down. As a rule, they are almost always barren; that is, they contain no valuable metals, and therefore make no compensating return for the fuel required to heat them, all this heat being lost when the slag is poured over the dump.

20. Loss of Lead in Slags.—It is impossible to completely separate the base bullion and matte from the slag; other things being equal, the greater the amount of slag, the greater is the loss at this point. This loss is more serious than one would suppose, because it is usually expressed in percentage with reference to the slag. But suppose, for the sake of example, that the charge is such that the slag produced weighs 10 times as much as the lead produced, and that it contained three-fourths of 1 per cent. of lead, a not unusual ratio. Now suppose the slag to be reduced until it becomes 8 times the weight of the lead, with no change in the percentage of lead in the slag; this will result in an absolute saving of 1.5 per cent. of the total quantity of lead charged.

21. Quantity of Lead for a Charge.—The charge must contain at least a certain percentage of lead, in order to work well in the furnace; and with the same ore an increase of fluxes means a reduction of the percentage of lead in the charge. In districts where lead ores are scarce and where the lead is used primarily as a collecting agent for gold and silver, this point is an important one.

The barren fluxes occupy room in the furnace that should, if possible, be utilized for ore. The tonnage of the furnaces will be the same, other things being equal, for a small or large proportion of ore in the charge; and the cost per ton of charge smelted for fuel, labor, interest, and depreciation

of plant will be the same whether that ton contains 1,200 pounds or 1,600 pounds of ore.

22. The flux added should be the lowest-priced material of its class that will give the desired properties to the slag, but in general it is a false economy to save on the cost of fluxes at the expense of having the capacity of the furnace reduced a third or even a half by irregular working.

The desired fusibility can best be obtained with a given amount of flux by using two or more bases to combine with the silica instead of only one.

23. Fluxes Suited to Smelting.—Of the bases available, two have been found, by years of experience, to be eminently adapted to the situation, namely, ferrous oxide FeO and calcium oxide CaO. Iron, in the presence of lime, tends to make the slag readily fusible, fluid when fused, and high in specific gravity; if in excess, it is liable to form crusts in the furnace. It has been ascertained that in a pure ferrous silicate, if the iron be replaced little by little up to a certain point (in the neighborhood of 15 per cent. CaO for a singulosilicate) the formation temperature is lowered by such additions. Above this point it begins to rise again. This, of course, is in conformity with the statements made that a silicate of two bases is more fusible than a silicate of only one base.

The effect of lime on the specific gravity of the slag is to decrease it. It will be seen, therefore, that by varying the proportions of lime and iron in the slag the specific gravity may be varied in accordance with certain laws. The fusibility also can be varied according to the principle indicated by the change brought about by replacing iron by lime in the manner described. In practice, the variation of these two properties in this manner is exactly what is done.

24. 20, 30, 40 Slag.—On the other hand, an increase in the proportion of silica SiO_2 above a certain point diminishes the fusibility, and the composition of the desired slag is based upon calculations that take into account the effects of these three materials. In general, the proportion of silica

is such that the composition of the slag will approximate a singulosilicate. A combination that has given excellent results is the following: CaO, 20 parts; SiO_2, 30 parts; FeO, 40 parts; total, 90 parts, leaving 10 parts to be made up by other substances, such as aluminum oxide Al_2O_3, zinc oxide ZnO, etc. For smelting clean average ores, this would

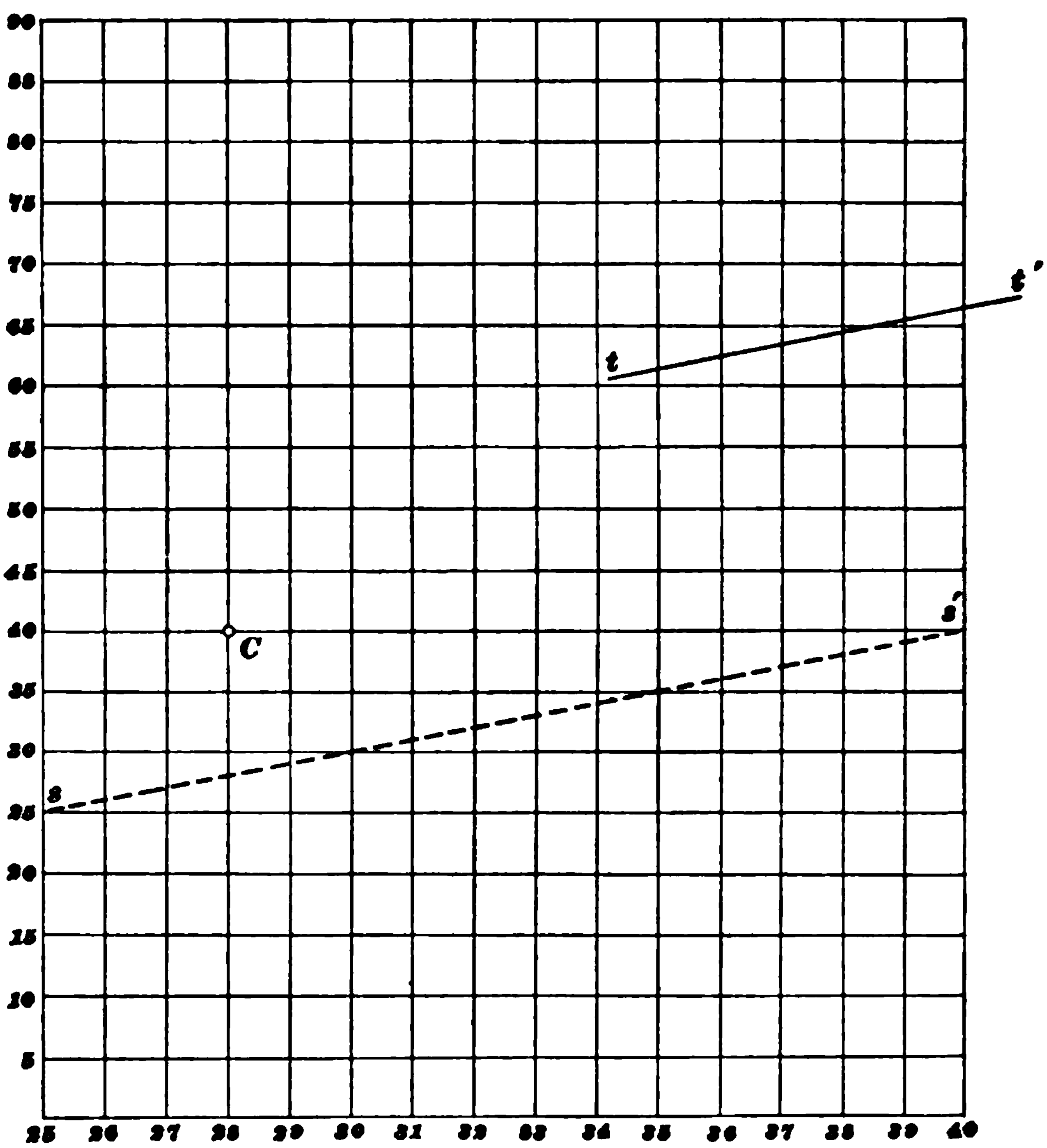


FIG. 5

undoubtedly give good results, but the question of economy comes in. Iron ore usually costs more than limestone, and both are dead weights at best, so the aim of the modern smelter is to force the slags as high in SiO_2 and as low in FeO as may be found consistent with the good running of a furnace.

25. Slag Diagrams.—It must not be imagined, however, that the problem of slag composition is as simple as might be inferred from the foregoing. In many respects it is not only decidedly complex, but also obscure as to the laws that govern and control the various properties, both desirable and undesirable. In fact, it seems to be well established that the composition of the desirable slags follows certain definite lines, and the accompanying diagram, Fig. 5, shows one attempt to get at the definite laws that must underlie the action and effect of the various ingredients. In the first place, it might be supposed that if two slags of slightly varying composition were good, that any composition intermediate between these would yield a slag equally good, but it has been found that such is not necessarily the case.

In Fig. 5 a number of slags that have been found, by experience, to work well have been located according to the following system of coordinates: The line $s\ s'$ is so drawn as to represent parts of SiO_2 on both vertical and horizontal scales. That is, if, for instance, it is desired to express graphically a slag containing 35 per cent. of SiO_2, it is found that the line $s\ s'$ intersects the vertical line corresponding to that composition, and upon which the point must be located, at the same point that this vertical line is intersected by the horizontal line also representing 35 per cent. If, then, the point is so located on this vertical line that its distance above $s\ s'$ will represent the percentage of CaO present, the distance from the point to the horizontal line corresponding to 90 per cent. will represent the percentage of FeO present; that is,

$$90 \text{ per cent.} - (\overset{35}{SiO_2} + \overset{25}{CaO}) = \overset{30}{FeO}$$

it being assumed that these three components make up 90 per cent. of the total slag composition.

26. It is generally believed that the nearer an approach is made to some molecular compound, the better will be the slag; but there is great uncertainty as to what are the definite

compounds that form good slags. It is, however, practically impossible to so calculate the charge that the slag when analyzed will do better than come within a fraction of 1 per cent. of the composition aimed at, and since this is the case, any attempt at too great refinements in the matter of slag composition is a loss of time. For the average furnaceman, the best that can be done is to select some type that has proved itself good in practical working and is of the approximate composition that his conditions require, and then to conform his slag to this as nearly as may be possible.

Reference has already been made to the slag known, for the sake of brevity, as the 20, 30, 40 slag, and, as stated, this would be desirable but for the sake of economy. The aim at the present time, however, is to force as much silica as possible into the slag and also to make the proportion of lime to iron as high as it will bear, so that a more representative composition would perhaps average more nearly 32 per cent. of silica, or even a little higher, 36 per cent. of iron, and 22 per cent. of lime. Such a slag lies about half way between the singulosilicate and the sesquisilicate types.

27. The practical limits for the three principal components are as follows: Silica, 28 to 36 per cent.; lime, 10 to 30 per cent.; iron, 24 to 52 per cent. (Ile's slag). The actual properties of a good slag are, perhaps, worth stating. According to one authority, who has given this subject careful study, the requirements of such a slag are that it should not contain over three-quarters of 1 per cent. of lead or ½ ounce of silver to the ton, with base bullion running not higher than 300 ounces to the ton; nor should it have a specific gravity greater than 3.6. It should not form hearth accretions nor should the furnace run with a hot top when it is in use.

28. It is believed by some that when a slag shows a crystalline structure upon cooling it is evidence that a definite chemical compound has been formed, and that it is, therefore, a more desirable slag than one that exhibits no

such crystalline structure. In some works especial stress is laid upon the appearance of a columnar structure when a cone of solidified slag is broken, the columns being formed vertical to the position in which the slag is cooled. It is claimed that the slag is much cleaner, that is, freer from lead, when this particular structure exists, and that it is much more in evidence when the proportion of lime to iron is expressed by some simple ratio, as, for instance, 1 : 4, 2 : 4, or 4 : 4, and the slags are correspondingly known as $\frac{1}{4}$ slags, $\frac{2}{4}$ slags, $\frac{4}{4}$ slags, etc.

According to other authorities, however, the excellence of a slag showing evidence of crystallization does not appear to be by any means invariable, and most smelters aim to make a certain type. Then, by experimentation, attempts are made to increase slightly the percentage of silica and the proportion of lime to iron until it is found that a practical limit has been reached. This practical limit will vary decidedly with other conditions, which cannot by any means be definitely determined.

29. Recapitulation of Slags.—The principal action of iron, which, it is to be remembered, *must always be present in the slag in the ferrous state*, is to form a base for combination with the acid silica; it also plays a small part in the liberation of metallic lead from sulphide or silicate of lead. The effect upon the slag of an increase in iron is to render it more fusible, more liquid, and higher in specific gravity. Putting aside the question of cost, therefore, up to a certain point iron is desirable, though it is not to be forgotten that it is quite possible for a slag to be too fusible. But when it causes the specific gravity to become excessive, it prevents a clean separation of the lead from the slag and therefore becomes objectionable. If increased too much, it is liable to cause the formation of crusts. In the case of zinc ores it assists in the removal of the zinc in the slag.

30. Manganese acts in a manner almost identically with iron. Its tendency, however, is to give unlooked-for oxidizing effects, on account of the fact that it is almost

always present as pyrolusite MnO_2. In calculating a slag, manganese is considered as directly equivalent to iron, since its atomic weight is so nearly the same, *Fe* 56 *Mn* 55, and its properties correspond so closely.

31. Lime acts similar to iron as a base to satisfy the acid silica. Its tendency is to decrease the fusibility in proportion to its increase with reference to iron, after reaching a certain point, which is shown in Fig. 5. The increase of lime also decreases the specific gravity and, consequently, tends to produce cleaner slags. *When zinc oxide is present, however, the amount of lime must be correspondingly decreased.*

32. Magnesia is generally calculated as lime in making up a furnace charge; due allowance, however, must be made for the difference in atomic weight. As a matter of fact, more than a small percentage of magnesia gives much trouble in the blast furnace; by its refractory nature it causes the slag to be pasty and consequently to lack homogenity; dolomites, which carry 45 per cent. of magnesia carbonate, are therefore to be avoided as blast-furnace fluxes.

33. The part played by **alumina** in the slag is one that is in dispute. By some it is claimed to act as an acid, by others as a base; certainly all known indications point to the fact that under some conditions it acts as the one and under other conditions as the other. Nothing definite is known as to the real reasons causing the change in its relations to the other elements present.

Some success is had at times by considering it as taking the place of one-half its percentage of silica. One fact does appear with unpleasant prominence: when alumina and zinc are both present, it is impossible to run successfully if the slag contains more than 7 or 8 per cent. of alumina. Even when zinc is absent, alumina is undesirable in quantities above 8 per cent.

34. Zinc is the most objectionable of all the elements liable to appear in the slag. Its composition, when present,

is in doubt, but most of the evidence seems to favor the theory that it is present largely as zinc oxide in solution and that the ferrous silicates are the compounds most active in effecting such a solution. It is certain, in any event, that an increase in the proportion of iron renders the zinc more easily handled. Where it is necessary to run the slag high in this metal, the iron must be correspondingly increased or the lime decreased, which amounts to the same thing.

The effect of zinc is to cause accretions to form in the furnace and to render the slag pasty. It is especially objectionable from the fact that it always tends to carry silver into the slag; thus, while it is possible to run a slag as high as 12 per cent. in zinc, in such a case 2 ounces of silver per ton have been found in the slag. When alumina also is present in any amount, it is rarely if ever found practicable to increase the percentage of zinc above 7 or 8 per cent., both on account of the formation of accretions in the furnace, due to the partially fused condition of the slag, and because the losses of silver become prohibitive.

EFFECTS OF OTHER ELEMENTS ON BLAST-FURNACE RUNNING

35. Sulphur.—From the nature of lead ores and the difficulty of removing **sulphur** completely by roasting, it is an almost invariable component of the charge in the blast furnace to a greater or less extent. A certain elimination in the furnace always occurs through the formation of sulphur dioxide SO_2, according to reactions already given, but a further amount is practically certain to make its appearance at the tap hole in combination with iron and copper, if they are present; this compound is known as **matte** and carries with it more or less lead.

The presence of matte, especially if in too large a proportion, is not usually considered desirable, because it carries with it a certain amount of the gold and silver, and since the matte requires reroasting and resmelting, it becomes the agent of increased expense and possibly of loss; but it is by

no means to be considered an unmixed evil. In fact, it acts in one sense as a safety valve and allows a certain latitude in the strength of the reduction permissible in the blast furnace. If no matte were possible, it would be essential to bring about just such a reaction as would result, on the one hand, in the reduction of all the oxidized compounds of lead, and on the other hand it would leave all the iron in an oxidized condition; because if metallic iron were formed in the blast furnace, it would appear in the hearth in the form of accretions of a most objectionable character. Since the matte is present, however, it takes care of any slight variations from this line and renders it possible to reduce all the lead; to be sure, some of it appears in the form of sulphide in the matte, but since this is to be resmelted it would not be lost, as would be the case if the lead were left in its oxidized form and therefore entered the slag.

36. Arsenic is of frequent occurrence in ores that are to be smelted in the lead blast furnace and gives rise to two principal difficulties. It may be volatilized either as metallic arsenic or as some of its volatile compounds, or it may unite with reduced iron to form a series of compounds corresponding to the sulphides of iron and having the form $FeAsS$.

If the arsenic is volatilized, losses of lead and the precious metals are involved, while if speiss is formed, it may give much trouble by the formation of hearth accretions. Consequently, if arsenic is present in large amounts, since the losses by volatilization render that method of disposal prohibitive, it is necessary to so run the furnace as to bring about the combination of the arsenic with iron. If this is done in such a way as to form the speiss corresponding to the symbol Fe_6As, the product is much more fusible and liquid than if the ratio varies from this type in either direction. To form just the compound aimed at is accomplished by regulating the amount of iron ore entering the charge and by varying the reducing power of the furnace, which is dependent on the combustion of the fuel.

If speiss is being formed, it is highly desirable to keep the hearth temperature high, since under the most favorable circumstances it is none too fusible. This is brought about by the use of a slag with a comparatively high formation temperature. If, however, the amount of arsenic present in the charge is small, it will probably be found more advantageous to prevent the formation of speiss, thus forcing the arsenic either to volatilize or to combine with the lead. This may be accomplished by lessening the reducing power of the furnace and consequently producing no excess of metallic iron with which the arsenic may combine.

It is also stated that a reduction in the lime component of the charge has a similar effect, because it forces all the iron into combination with the silica and leaves none for the arsenic; but even in this case it is probable that variations in the reducing power of the furnace would be found to play a considerable part.

37. Antimony may in some exceptional cases combine with iron and form an **antimonial speiss,** but in general it is either volatilized or appears in combination with the base bullion, making the latter hard. Neither action is desirable, but the last-named is the lesser evil, since the ultimate loss is less and it is possible to recover the antimony directly and in a marketable form, while if it goes over as flue dust it must again and again enter the base-bullion blast furnace, giving rise to the constant recurrence of the difficulties connected with its presence there.

COMPARISON OF METHODS AND SPECIAL DETAILS

38. Ore Bedding.—There is not much room for variation in the details of this process. The best method of doing it by hand is to run the cars containing the ore directly alongside the bedding bins and to sample by fractional selection, throwing the rejected portion into the bin at once.

A very effective method of automatic bedding is provided by the use of the automatic dumping car shown in Fig. 6. In its application to this purpose the ore is discharged from the railroad car by means of a chute into the dumping car. The latter runs on an inclined track placed over the center of the bedding bin. When the car is full it is liberated and descends the incline until it reaches a stop, which causes the car to discharge. With this stop is connected a spring,

Fig. 6

which is extended by means of the momentum of the car; as soon as the ore is discharged the spring snaps the car back into its original position beneath the chute, since its weight has been decreased by the loss of its load of ore. It is then ready to receive another load. The stop is arranged to travel automatically along the line of track so as to distribute the ore uniformly; a certain amount of hand spreading is, however, necessary, but by the use of V-shaped ore

spreaders beneath the car this may be reduced a very small amount and the manual labor necessary very much decreased.

39. Making Up Charges.—The simplest manner in which this can be accomplished is by means of iron wheelbarrows, shown in Fig. 7, and these are used very largely

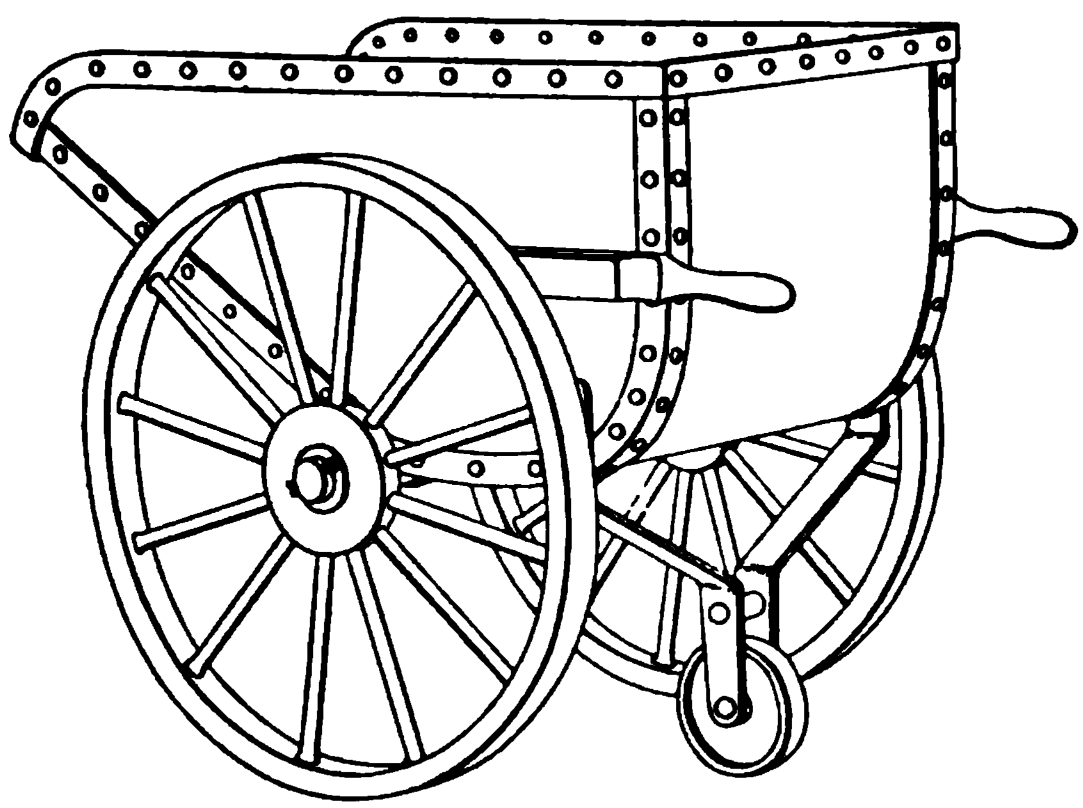


FIG. 7

for ores and fluxes. For coke a special car is almost always used, and one form is shown in Fig. 6. In more advanced works special ore cars have been introduced in which to transport ore and fluxes and the charge as calculated is, to a considerable extent, assembled in this. Each wheelbarrow load of material is weighed as it is dumped into the car, which, after its charge is complete, is then run on a tramway passing at a slight elevation the feed holes of all the blast furnaces. When the furnace for which the carload is destined is reached, the car is dumped upon the charging floor.

BRIQUETTING FINE ORES

40. If too great a proportion of the charge is made up of fine ores, the blast will not be evenly distributed, and blowholes and irregular working of the furnace will result, leading ultimately to the loss of considerable amounts of

dust carried away by the blast and the formation of accretions within the furnace. Ores from mechanical roasters

FIG. 8

or those that have been through fine crushing machines for the purpose of sampling concentrates and other ores that

are received in a state of fine division will, when introduced into the blast furnace, pack more or less.

It is in order to avoid these difficulties that, when the ore is roasted in a hand reverberatory furnace, it is either sintered or slagged at the conclusion of the process; but since either of these operations is impossible in mechanical furnaces, some other method must be adopted to cause a proper proportion of the charge to be in the lump form. Up to the present time the best means for effecting this is to compact the fine ores into briquets by some one of the various machines for the purpose on the market.

41. Briquet Presses.—The White mineral press, shown in Fig. 8, requires a thorough mixing of the material, and the briquets themselves must be carefully handled after they are manufactured, otherwise they are not sufficiently strong to serve the purpose for which they are intended.

The briquet press shown consists of a pan *a* fastened to a bedplate *b*, which in turn is firmly bolted to a masonry foundation *c*. There is a centrally located upright shaft *d*, moved by gears, which are not shown. Upon the upper end of this shaft is a yoke *f*, held in place by the bolts *g*. From this yoke extend arms *h*, that act as axles for two heavy chasing wheels *i*, which revolve in the pans. When the machine is at work, the arms *h* turn the hub *j*, which is made in the yoke *f*; in other words, the arm *h* has two axles, one at either end. The flat metal disk *k* revolves horizontally so as to form part of the bottom of pan *a*. In this disk are molds *m* that extend around the disk in pairs a few inches from its circumference. As the wheels *i* revolve, they press the matter in the pan into the molds, and as the disk revolves, an arm *o*, supplied with two plungers, presses the briquets *n* from the mold upon a traveling belt.

In one instance where a machine of this type is used successfully, the briquets are taken from the belt and stacked up in open rank to permit them to dry thoroughly in the air; but the expense and labor is a drawback to the operation. An attempt was made to dry them by waste

FIG. 9

heat, but on account of the faulty construction of the drier, it was abandoned for air drying.

42. The machine shown in Fig. 9 is a 6-mold briqueting press. The briquets made by this piston type of machine are dense and firmly constructed, consequently can stand handling. There is one plunger for each mold, but all plungers are operated by a heavy crank *a*, which is connected to them by a heavy pitman *b*. The plungers work against other plungers *c*, held in place by heavy coil springs not shown, but having a resistance of 75 tons with from $\frac{3}{8}$-inch to $\frac{3}{4}$-inch movement. The material fed through hopper *d* is compressed through a mold and passes to the endless belt *e*, in the form of briquets *i*. The binding material in this case is lime, which is slaked in trough *k* and mixed by the stirrers *m* until it is of the consistency of thick cream. This mixture is fed automatically by the apparatus *n* into the pug mill *o*, where it becomes thoroughly incorporated with the fine ore. The blades of the pug mill work the ore mixture forwards on to the belt *s* that delivers it to the hopper *d*.

43. In order to thoroughly bind together the material of the briquets, some cementing agent, such as slaked lime or zinc sulphide, is used. The lime is no drawback, since it merely replaces an equivalent amount of limestone, which would otherwise be used as flux. The zinc sulphide in itself would be objectionable, but in some cases the dust collected from the waste gases of the blast furnace contains, besides the lead and varying amounts of gold and silver, a very considerable percentage of zinc sulphate. Since this flue dust must be used in order to recover its values, the well-known binding property of the zinc sulphate contained in it is utilized to cement together the particles of ore. The use of molasses as a binding agent has been suggested and tried, but has not become at all general.

It would seem that some form of briqueting machine must become indispensable to all works where mechanical roasters are used. The advocates of the hand roasters claim

that they secure their ores in lump form at no greater expense than that involved in the use of mechanical roasters plus briqueting machines, to say nothing of all the other advantages to be found in hand roasting.

44. Charging.—Various arrangements of the order in which the materials composing the charge may be introduced into the blast furnace are in practice, each having its own advocates. The only special points to be brought out in this connection are that in most instances it is desirable that the coke should be covered by other portions of the charge in order to prevent its oxidation before it has reached a position in the furnace where this oxidation can produce the best effects. Some authorities lay stress upon placing the ore and flux in such a manner that the acid material will come next to acid and basic material next to basic as far as possible. In this way, it is claimed that the formation of the slag is prevented until the region of highest temperature has been reached.

There is undoubtedly great benefit in delaying the formation of the slag as long as possible for the following reason: If the arrangement of materials is such that a slag with low-formation temperature may be produced by the combination of materials lying nearest one another before these materials have time to absorb much heat, the slag, being liquid, drops rapidly through the lower and hotter portion of the furnace. This means that the hot gases of the furnace are allowed to escape without giving up as much of their heat as is desirable from an economic standpoint. On the other hand, if the arrangement of materials is such that the slag which the adjacent particles would form has a high formation temperature, these particles will descend with the rest of the charge gradually and uniformly through the furnace, absorbing more and more heat in passing until the hottest portion of the furnace has been reached, when they finally fuse. In this way ample time is allowed for the absorption of heat of the furnace gases, and these emerge from the top reduced in temperature, having accomplished their full work. The effect upon

the hearth temperature is obvious. If the slag was formed at a low temperature, it dropped rapidly to the crucible, carrying with it very little more heat than was necessary for its fusion. On the other hand, if the formation temperature was high, the slag would of necessity carry with it a much greater amount of heat.

The temperature of the hearth is maintained almost entirely by the heat brought to it by the descending molten material. Little, if any, heat is imparted by radiation from the combustion taking place at the tuyere level, for slag is a very poor heat conductor. For many reasons it is highly desirable in most instances that the hearth should be maintained at a high temperature, and as has been shown, this can only be effected by the means described. Whether, however, it is possible by a mere arrangement of the material of the charge to bring about this desirable condition is certainly open to question. The probabilities are that in its descent through the furnace the materials of the charge are mixed and that the original arrangement is largely, if not entirely, destroyed by the time the zone of fusion is reached. The only certain means of producing high hearth temperatures would seem to be in so calculating the components of the charge that the slag formed must have a sufficiently high formation temperature.

45. Mechanical Charging.—In only one instance has a successful attempt been made at automatic charging. In this case all the materials for a charge are assembled in a car with a drop bottom. The car is loaded at the foot of an inclined track, the lowest part of which is depressed below the level of the floor upon which the materials are assembled. These are weighed in wheelbarrows and each component then dumped directly into the car until the complete charge has been made up. The coke is put in last, in order to avoid crushing as much as possible. The car is then hauled up the incline by a wire rope, as shown in Fig. 10, and stopped directly over the mouth of the furnace for which the charge is intended. The car and the track upon

which it runs are made sufficiently wide, so that they may pass directly over the feed openings of the furnaces. Except when ready to receive a charge, these openings are closed by hinged doors of sheet iron, which are in a horizontal position, and can be dropped inwards when a charge is to be received. The bottom of the car has the shape of an inverted V, so that when discharged its contents may be distributed on either side The line forming the apex of the V lies parallel with the longitudinal axis of the furnace.

FIG. 10

By this means the charge is fairly well distributed, but to effect its more complete distribution, three angle irons are placed, apex up, directly across the shaft at right angles to its longer dimension and at a distance of about 18 inches below the feed-door. Of course, the furnaces must be of the type having the feed opening set in the charging floor, so that the car containing the ore may drop it directly into the furnace.

The desirability of this method of feeding is somewhat open to question; according to some authorities, a furnace charged in this manner could not work at all, but that it does is a fact that admits of no dispute. As to whether the furnace works as satisfactorily as in the case of hand charging is a question that can only be answered by testing the two methods side by side, with other conditions exactly similar. Certainly the attempt at reducing the amount of hand labor in connection with the metallurgy of lead is one that should be tried thoroughly and, doubtless, means can be found to insure its successful working.

46. The fuel must meet two requirements. It must be sufficiently strong to support the charge above it without crushing until it has reached the zone of combustion, otherwise it will become a mass of powder, which cannot be properly burned and which is liable to be blown out of the furnace as flue dust or to become mixed with slag, in which form it may cause troublesome accretions. The fuel must also be porous, so that when the zone of combustion has been reached, it may burn quickly and completely.

Charcoal fulfils the latter condition to a greater extent than any other fuel, but it rarely, if ever, meets the former requirement; further, it is difficult in very many localities to obtain a charcoal of good quality. With the increase in the height of the lead blast furnace, the lack of strength on the part of charcoal renders it less and less useful as a fuel for this purpose and coke has become practically the only fuel used in this country.

In some cases a small amount of bituminous coal has been introduced into the charge with fair results, but the hydrocarbon gases produced by its distillation are given off in the upper part of the furnace and are consequently nearly all wasted as far as the production of available heat is concerned. The net result is practically the same as though an equivalent amount of coke had been charged, while the formation of these gases leads to the possibility of dangerous explosions in the flues and dust chamber. It would seem,

therefore, that the only advantage in the use of bituminous coal would be that previous coking is not required, while the disadvantage due to the combustible gases is serious and one that necessitates the greatest care and closest watching. Anthracite coal is not desirable on account of its slow combustion.

47. Coke for Lead Smelting.—The coke used in a lead furnace need not have as great strength as coke that is to be used in the iron blast furnace, since the column of material that it has to support is so much shorter. An inferior coke can, therefore, frequently be utilized with good results. The great drawback to poor coke is that the amount of ash is usually high and must be taken care of in the slag, but the question of its use is one entirely dependent on relative cost. Strange as it may seem, it is possible to use too good a coke; for while it may be necessary to use a larger weight of inferior coke to secure the same reducing power, it has a very decided value in opening up the charge, and if too much good coke is used, the reducing action may be increased to such a point that metallic iron will be formed in the furnace in excess of all requirements for the reduction of lead sulphide and thus be left in a free state to cause accretions.

48. The percentage of fuel used in lead blast furnaces varies somewhat; the lowest figure that is practicable, if the furnace is to be kept in good condition, is probably in the neighborhood of 12 per cent. From this it runs up to 14 per cent. and in high altitudes even to 16 per cent. The cause for an increased consumption of fuel in high altitudes has never been satisfactorily explained.

With charcoal, although the loss due to ash is less, the amount of fuel that is imperfectly consumed is greater on account of the greater formation of carbon monoxide in the upper part of the furnace and the percentage of charcoal necessary for a charge may run higher than 20 per cent. In speaking of fuel percentages, it is to be understood that the fuel charged forms so many per cent. of the total weight of ores, fluxes, and old slags to be resmelted.

49. Blast Pressure.—While the question of blast pressure has already been touched upon, it is desirable to discuss a little more fully the points that would be involved in an increase of pressure. If this is effected without any change in the charge or in the size or shape of the furnace, it is soon found that the greater velocity of the air entering the furnace rapidly carries the heat higher up and the coke begins to burn before the charge has descended to the contracted portion of the furnace, where combustion takes place most effectively as far as both the physical and the chemical effects upon the ore are involved. If this extension upwards of the zone of combustion is carried too far, it is likely to cause over-fire or hot top, and with this condition there are the additional drawbacks of loss of heating power, greater volatilization, and an increased amount of flue dust—its invariable associates. In order to meet these difficulties, the percentage of fuel is decreased and by this means the zone of combustion is restricted to the region designed for it, and naturally an economy of fuel results. Even with a slight reduction in the fuel charge, however, it is found that an increase in the height of the furnace, which means that the gases must come in contact with a larger amount of charge before they are permitted to escape, is most desirable.

50. A similar restriction of the zone of fusion is effected by using a slag with a somewhat higher formation temperature, and this has the further desirable effect of utilizing to the utmost the heat of combustion of the fuel for maintaining the hearth temperature, as was shown in a discussion of this point. Such an effect upon the slag is gained by increasing the amount of lime and is one of the reasons for the fact that higher lime slags are now used than formerly. With such changes, namely, increased height, greater blast pressure, less fuel, and more lime in the slag, it is found possible not only to smelt more ore per day, but also to produce cleaner slags. It is probable that the limit of blast pressure has not yet been reached; some metallurgists are desirous

of testing the effect of a 3-pound blast, with other conditions arranged accordingly.

51. Hot Blast.—One point in which the metallurgy of lead has made no advance is the one in relation to the preheated blast. The hot blast has been utilized with success as far as the recovery of lead is concerned, but without gain from an economic standpoint. The great reason why the subject has not received more attention is because of the character of the waste gases. In the case of an iron blast furnace these contain a very large percentage of carbon monoxide; in the lead blast furnace, however, carbon monoxide is not present to any appreciable extent, the fuel being burned almost completely to carbon dioxide, therefore no more heat can be obtained from them than that which they carry physically—that is, they have no chemical energy in reserve. This does not preclude the possibility of the utilization of an inferior fuel for the preheating of the blast, and a field is open for improvement in this direction; whether the improvement can be made more than theoretical remains to be seen.

52. Tapping Slag and Matte.—Few variations are possible in these operations. Sometimes two tap holes at different levels are made in the tapping jacket to give some latitude in the level at which the molten material can be drawn out of the furnace, but this is not common. Occasionally furnaces have been made with tap holes for slag and lead at both front and back. The advantage sought is that the furnace is always more open at the end at which tapping is effected, because the flow of slag tends to remove any incipient obstructions and the furnace is also more readily accessible from without; but this method is open to the very serious objection that in almost all cases it is found necessary to reserve space at the back of the row of furnaces for handling the base bullion; and in addition it would be decidedly inconvenient to arrange the tapping floor on both sides of the row of furnaces. The advantages gained would

hardly be sufficient to compensate for the disadvantages incurred.

53. Separation of Slag and Matte.—The slag and matte are always tapped together on account of the impossibility of making any clean separation in the furnace. The external separation then becomes a matter of importance, since the matte always carries considerable values in lead, gold, and silver, and sometimes in copper.

The simplest method of separation is to allow the matte and slag to flow together into an ordinary slag pot. When full it is wheeled away and allowed to cool. The cone of slag and matte that accumulated at the bottom can be readily broken off. Fig. 13 shows a number of slag cones with the matte broken off.

The most common method of effecting the separation, however, is to allow the molten materials to flow together from the furnace directly into a large iron box, with detachable sides, lined with firebrick, and mounted on wheels, termed a *forehearth*. In this the exterior of the mass of slag is chilled and a shell is formed at the top, bottom, and sides, but the interior remains molten and will continue so for a considerable length of time, slag being a very poor conductor of heat. The crust that forms over the top is kept open in two places—at the end of the box, where the stream of slag and matte from the furnace enters, and at the end, where clean slag overflows into the slag car, as at *a*, Fig. 11. The length of time involved in passing through the forehearth is sufficient to allow nearly all the matte to settle out by virtue of its greater specific gravity and to sink to the bottom. This matte also remains molten and is drawn out from time to time, ordinarily about once an hour, through a tap hole *b* provided in the side of the forehearth, near the bottom. This tap hole is kept from freezing by means of an iron rod *c*, which is inserted in it before any slag is allowed to flow into the forehearth. The time for tapping the matte is ascertained by introducing a cooled iron rod through the opening in the shell of slag at the top and noting the depth of the

matte that adheres to the rod. The rod closing the tap hole is loosened by means of a sledge, then pulled out and the matte allowed to flow until it has been nearly, or quite, all removed. The tap hole is then plugged with fireclay and the iron rod at once driven through to the molten interior before any freezing can take place.

FIG. 11

54. The slag that overflows from the forehearth still contains some matte, which will settle to a large extent and be found either in the shell of slag that is chilled by contact with the iron pot *a*, placed in the ground, as shown in Fig. 12, or near the bottom of the portion that remains molten.

In Fig. 12 is seen a slag pot *b* that has been filled from the overflow of the forehearth and is being dumped into a slag pot placed in the ground. The slag pot *a* is provided with bales *c* for the purpose of lifting it by the traveling

crane *d*. A tap hole is placed in the side of the slag pot through which the molten slag is drawn, so that practically all slag drawn is free from lead and matte, and may be removed to the dump. In the illustration, *f* is the slag pot being tapped into a slag car *e*. The shell of hardened slag and the small amount of matte remaining at the bottom are separated as shown in Fig. 13. The thin shell of slag that

Fig. 12

comes from the pot is afterwards broken up and returned to the furnace for resmelting, and in this way a supply of slag is obtained to use in making up the charge.

55. The advantages of this practice are that the slag returned contains to a large extent all the values that have escaped from the forehearth. Sometimes an ordinary slag pot without tap hole is used, the liquid slag being poured out and merely the shell retained.

Varying types of forehearths and slag pots are used at different smelters; in some cases this is necessary in order to comply with peculiarities in the construction of the furnaces; in others they are merely to meet the fancy of the superintendent. A forehearth is used until it freezes up to such an extent that its capacity is too seriously lessened to

allow a proper separation of slag and matte. This may take 1 day or 1 week, but when it does occur, the forehearth in use is replaced by a fresh one. The forehearth that has

FIG. 13

chilled is wheeled away and allowed to cool, after which the sides are let down and the matte broken loose, as shown in Fig. 14.

56. A much more elaborate method of separating the slag from the matte and one that results in the most perfect recovery of values that would otherwise be lost, is that in which all the materials flowing from the slag pot are carried directly to a reverberatory furnace with a deep hearth, poured into it, and allowed to settle there for several hours; that is, the capacity of the reverberatory hearth is great enough to contain all the slag that will be made in such a length of time. The slag is maintained in its molten condition by the flame of the furnace, and lead and matte that have been carried mechanically are afforded the best of

conditions under which to settle out by virtue of their greater specific gravity.

In the hearth are three tap holes, one near the upper level for slag, which is allowed to flow nearly continuously, two at slightly different levels near the bottom of the furnace and on the opposite side are utilized to tap out base bullion and matte that accumulate beneath the slag. These materials are tapped into suitable pots at intervals which are determined by the rate at which it is found by experience they accumulate there. The shells that remain in the slag pots

FIG. 14

used to carry the molten slag from the blast furnaces to the separator are utilized, as in other methods, for making up a portion of the blast-furnace charge. While this type of separator may be much more expensive in the first cost than any of the other methods in use, the results obtained by it are so eminently satisfactory that at some works it is not considered good policy to do without their services for even so short a time as is necessary for the occasional repair of the reverberatory, and it is, therefore, thought worth while to hold a duplicate separator in reserve. The values

thus recovered are surprising, but the figures cannot be given here.

57. Tapping Base Bullion.—The molten base bullion may overflow continuously from the lead well that forms the

Fig. 15

termination of the Arents siphon tap into an external iron kettle; or it may be confined in the lead well by building up the sides somewhat and closing the channel through which it

overflows by means of fireclay, which is removed occasionally and a certain amount of lead drawn at one time into the external kettle.

Casting base bullion is done from the kettle. The old method was to ladle it out by hand into iron molds, which are of the shape shown at *a* in Fig. 15. A great improvement upon this method is that which provides a tap hole *b* near the bottom of the kettle *c* through which the molten base bullion can be drawn, while the bullion molds, placed side by side upon a truck running on tracks, are brought beneath the opening, filled and removed in succession. In this way the heavy manual labor necessitated by hand casting is avoided, and it is also possible for the workmen to avoid standing immediately over the kettle and inhaling the poisonous fumes of the lead. Base bullion from high blast furnaces is assembled in one large kettle, and may be brought to this kettle molten by means of a small carrier mounted on wheels, into which it is drawn directly from the lead well, or it may be cast into pigs according to the method last described, and then brought to the large kettle and remelted. In this large kettle much of the dross and impurities held mechanically rise to the surface and may be skimmed out, leaving the base bullion to a very great extent free from these undesirable materials, which, freed from metallic lead as completely as possible, are to be at once returned to the blast furnaces. The base bullion is drawn from this kettle by means of a siphon made of iron pipe.

58. By the utilization of this method, the bars of base bullion are obtained clean and nearly free from mechanically held impurities, while if the bullion is cast into its final pigs directly at the blast furnace a great deal of dross is liable to be enclosed. The advocates of the system under which the base bullion is carried molten to the skimming kettle claim that it is quite illogical to cast the base bullion into bars that are immediately to be remelted, and this would seem at first glance to have some weight; but

it has been found that the extra fuel required to melt down the bars over and above what would be necessary in any event to maintain the lead in its molten condition, is quite insignificant, while the advantages gained by doing all the casting into the final bars in the daytime, when labor is cheaper, more than compensate for the slight extra fuel, because the operations can be watched more closely and are likely to be more carefully conducted.

FIG. 16

59. Ventilation. — The fumes that are copiously evolved at both the slag tap and the lead well are very objectionable, and the latter especially are extremely poisonous on account of the lead that they contain. The men who cast the base bullion are very likely to have lead poisoning if the casting is done from hand ladles or if a means for the removal of the fumes is not provided; therefore, at many of the works at the present time a sheet-iron

hood *a*, shown in Fig. 16, is constructed directly over the lead well and another hood *b* over the slag tap connected with a main, from which the air is exhausted by means of a fan. These hoods vary in size from what is practically nothing but a small box of sheet iron enclosing the tap hole, with an opening left in the front through which the molten material can flow and the tap hole can be opened or closed, to much more elaborate constructions, which cover the forehearth and the space where the furnaceman stands. In such cases dependence should not be placed on the removal of the fumes by virtue of their heat, but they should be directly removed by means of fans. The poisonous fumes are also liable to rise to the charging floor immediately above unless special provision is made to keep them from going there. In one works a partition is especially constructed to shut off the gases completely from the charging floor.

60. Sampling Products.—Samples of the slag and matte are usually taken twice a day from each furnace, both in order to ascertain the condition of the furnace and also to keep track of how much lead, gold, and silver each class of products contains. The slag may be sampled by dipping it from the stream as it flows from the forehearth or by thrusting a clean, cold iron rod into the slag pot, withdrawing it at once, and chilling in water the coating that adheres. The matte is sampled as it flows from the tap hole in the forehearth.

In sampling the base bullion, two methods are in use. The first is necessary where the base bullion is cast into its final shape for shipment directly at the blast furnace and consists of driving half way through each pig from both top and bottom a punch of the shape illustrated in Fig. 17.

The punch is then given a blow on the side, which loosens it and breaks off the cylindrical

FIG. 17

chip from the pig, so that it may come away with the punch, to be dropped into a bucket.

Unfortunately for the purpose of sampling, it is found that the contents of silver and gold vary widely in different portions of the same bar. It therefore becomes necessary, in order to obtain a relative sample, to vary the location of the point from which the sample was taken in each successive bar; the customary method of effecting this variation is to sample at the points shown in Fig. 18, then turn the pig over and sample from the opposite side.

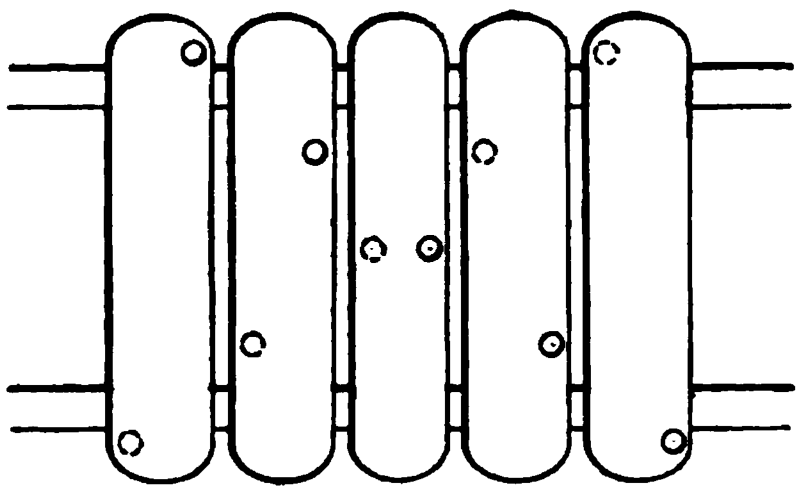


FIG. 18

This method of sampling is satisfactorily carried out by contract. All the bullion turned out is delivered to the contractor and his men at the cars upon which shipment is to be made and the punch samples are taken as the bullion is loaded. Under such a plan satisfactory results are obtained, it being found that three men can sample 600 tons of base bullion daily. When the chips representing a lot of base bullion have been collected they are melted down and cast into a flat bar, which is cut in two longitudinally; half is kept for the **control** or umpire's sample and from the remaining half four samples are cut for assay.

The second method is only possible where the base bullion is assembled in one large kettle in a molten condition before casting. In this kettle the base bullion becomes thoroughly mixed, and as it flows from the siphon used for casting a dip sample is taken by the man in charge of the casting. For this purpose the molder uses a small ladle, which he fills from the stream of molten metal. This procedure for every ten pigs cast is found to give a very correct and representative sample, besides simplifying the process and is, if anything, more accurate than plugging.

BY-PRODUCTS AND THEIR TREATMENT

61. Matte.—This may be considered a by-product, since its production is not the primary object of the smelting process. It is necessarily formed to a certain extent and is really quite serviceable in smelting for base bullion. The composition of the matte formed in a lead blast furnace varies much with the amount of copper contained in the ore. The greater part of this copper will reappear in the matte as cuprous sulphide Cu_2S. Associated with it will be iron sulphide FeS and lead sulphide PbS and possibly some other sulphides in much smaller amounts. This matte is roasted in the same manner as a sulphide ore and is resmelted in the lead furnace in order to recover the lead values that it contains. . The results of this resmelting are base bullion, slag, and a matte much higher in copper and lower in lead than the original matte. This is known as the **second matte** and may be smelted once more with a view to the recovery of further amounts of lead; its subsequent treatment is entirely on the basis of the copper values that it contains. Any gold and silver remaining will accompany the copper, and a discussion of the methods involved belongs more properly to the consideration of copper smelting. In some instances the matte is granulated as drawn from the forehearth. The granulated matte, however, does not appear to roast as satisfactorily as that which has been allowed to cool in solid cones or cakes, to be subsequently broken up in a crusher.

62. Speiss.—The amount of speiss produced is usually so small that no attempt is made to separate it from the matte, to the properties of which it conforms more closely than to those of any other product of the blast furnace. It is, therefore, roasted with the matte, and the arsenic is to a very large extent volatilized as sulphide in the process of roasting, so that comparatively little reappears as speiss with the second matte which is produced.

63. Flue dust is certainly not a desirable product, but it is nevertheless formed, varying in quantity from less than 1 to 10 per cent. of the ore charged; any quantity less

than 5 per cent. may be considered good furnace working. Flue dust results from the volatilization of lead, arsenic, antimony, zinc, and any of their volatile compounds that may be formed in the blast furnace; and it also contains fine particles of ore and fuel that have been carried mechanically from the furnace by the blast. Unfortunately it also contains a very considerable amount of the precious metals that, though not volatile in themselves, seem to be carried over mechanically in a state of extremely fine division by the other more volatile materials. In addition to the metals mentioned, flue dust nearly always contains a certain amount of sulphuric anhydride, a matter worth remembering, since it has a rather important bearing upon the recovery of the flue dust.

The collection and recovery of the material thus carried over from the blast furnace is a matter of great importance. The amount of lead volatilized is probably ordinarily underestimated, and unless efficient means of removing it from the waste gases before the latter are allowed to escape from the stack are provided, it may become a serious source of loss. Three points must be observed in effecting this recovery. The gases must be cooled, their speed must be reduced, and surface must be afforded upon which the suspended material may have an opportunity to settle out or condense.

64. The most usual apparatus for collecting flue dust is a system of long horizontal flues of large diameter. In some cases the total length of flue that must be traversed before the gases finally reach the stack is over a mile. The flues are built sometimes of red brick, sometimes of sheet iron, and in other cases of a special material, which has been named after its inventor, **Monier.**

Red-brick flues are the most durable as far as observations up to the present time extend, and are excellent if the capital is available to construct them of sufficient length. Their principal drawback is that they radiate heat with difficulty and their cooling effect upon the gases is proportionately slow. In the older types of brick flues, numerous sharp

turns and variations in size were introduced. The theory was that when the gases were forced to turn a corner opportunity would there be afforded for the particles to drop out, on account of the change of direction. It was also assumed that by suddenly increasing the size of the flue by the introduction of a chamber, the speed of the gases would be so diminished that again an opportunity for the dust to drop out would be afforded. The actual advantage of this method, however, is no longer accepted to any great extent, for it is found that the currents and eddies of gas caused by these means result in taking up the dust again and the net gain is very slight. It must not be understood from this, however, that an enlargement of the cross-section throughout the length of the flue is not an advantage; on the contrary, it seems to be one of the simplest and best methods for allowing the dust to settle out. The rate of flow per lineal foot must, of course, be reduced with increase in cross-section, and as the gases travel more slowly the opportunity for settling and condensation is correspondingly increased, so that in some of the most recently constructed plants flues of large cross-section have been introduced without any other devices for the recovery of the dust. In the construction of brick flues, numerous openings should be provided for entrance to the flues whenever cleaning and the removal of the accumulated dust is necessary.

65. Sheet-Iron Flues.—On account of the slow radiation of heat by the brick flues, sheet-iron flues have been introduced in some instances. These have been built in various forms, one of which is shown in Fig. 19. The construction of these flues is much simpler and cheaper than that of brick flues. Their great drawback, however, is that the radiation of heat is in some instances too rapid in a climate subject to great changes of temperature. While the sheet-iron flues may work well during the hot weather, in winter the radiation of heat proceeds to such an extent that the gases become too cold and the stacks can no longer produce the required draft. For a short system of flues, however,

the sheet-iron type has proved successful in many instances, particularly the form provided with numerous hoppers along the bottom. This shape not only prevents the dust which has once dropped out from being carried along by the current of gases, but also permits the frequent and easy removal of the material that has accumulated in the interior. If the draft should prove insufficient at times, this difficulty may be overcome by introducing exhaust fans.

FIG 19

66. The **Monier flues,** which are the most recent introduction, and are perhaps the most successful of all, if properly constructed, consist of a framework of wire netting or of expanded metal (sometimes known as metal lath and frequently used as a support for plastering) is stretched over supports and coated with a plastering made of cement and sand. Fig. 20 shows one of the largest of these flues built in this country, and its construction may be taken up in some detail. First of all, a foundation is laid for the

walls by running concrete into a trench *a* made of planks, as illustrated in the foreground. Upon this concrete foundation angle irons *b*, bent into the shape of a parabola, as shown, are erected and their bases surrounded by a further amount of concrete in order to support them more firmly. Over this the expanded metal *c*, which is to support the cement *d*, is stretched. Then layers of cement and sand are spread over this in such a way that the greatest thickness is outside the metal support. After the plaster has set and

FIG. 20

dried thoroughly it is coated on the inside with an acid-resisting mixture and the outside is painted. The flue under consideration has a cross-sectional area of nearly 300 square feet. Three lengths of 1,000 feet each were built side by side and so connected at the ends that any one of the three lengths could be cut out when cleaning was necessary. The advantages of flues of this construction are low cost, durability, and a proper radiation of heat, avoiding the comparative insulation of the brick flues and excessive radiation of sheet iron.

It should be noted that by the use of a cross-section thus shaped nearly the maximum area of cross-section possible with a given amount of material is obtained; and further, that party walls are avoided—an error of frequent occurrence and greatly interfering with the efficiency with respect to the cooling of the gases.

67. Collecting Flue Dust.—Further advances have been made in the collection of flue dust by the use of devices affording considerable surface in the interior of the flues upon which the material in suspension may settle and condense. For this purpose suspended wires—plates of sheet iron placed parallel with the direction of the gases, netting, etc.—have been used, and by thus increasing the surface exposed to the gases it is found possible to decrease very largely the length of flues through which the gases must be conducted in order to recover their valuable materials. But even these devices do not recover entirely the material that has been actually volatilized and which is known more specifically as **fume.** Even after condensation this fume is so extremely light and "fluffy" that in even the longest systems of flues it is apparently only imperfectly recovered.

In order to extract this more perfectly, in some instances the gases are forced to pass through filter cloths of loosely woven cotton or woolen material, and their use seems to show that without them a very considerable amount of valuable fume may be lost. Two methods of arranging the cloths are in use. In one they are stretched zigzag through a chamber and the gases are forced through them by means of a fan so arranged that the dust shall always accumulate on their under surfaces. The dust is removed at frequent intervals by automatic wooden beaters and conveyed to hoppers. It was found in a plant where this system was used that 7 per cent. of the lead charged into the blast furnaces was recovered at this point. The other system is that used in the production of pigment by the Bartlett process, and will be described under that heading.

68. Various attempts have been made to recover flue dust by systems of wet condensation. Among these are the introduction of jets of steam or water into the flues. To such methods two principal objections apply. In the first place, it is nearly impossible to wet the fume—as distinguished from the mechanically carried particles—and in this way a very valuable portion of the material is lost. In the second place, the gases always contain, besides sulphurous anhydrides, a certain amount of sulphuric anhydride, and when this latter combines with water, sulphuric acid is produced. The effect upon masonry, iron, and concrete constructions is then disastrous and no efficient way of controlling the acid waters has been devised.

Another suggestion for the recovery of flue dust has been in the use of discharges of static electricity. This method will throw down the material held in suspension if the gases are at rest, but no success has attended its application to the gases moving in a current.

BARTLETT PROCESS FOR THE TREATMENT OF ZINC-LEAD ORES

69. In the discussion of blast-furnace smelting of lead ores, it was found that zinc was one of the most objectionable elements that occurred in the treatment of lead ores. The removal of the zinc has been the subject of much experimentation and various schemes have been exploited, none of which has met with success.

Only one process is in existence which successfully treats lead ores running high in zinc, and while this recovers neither lead nor zinc in a metallic form, both are obtained in a marketable condition and the gold and silver contents are to a large extent recovered. The theory on which this process depends is that lead and zinc may both be volatilized in currents of hot air, while the gold and silver are retained to a considerable extent by a matte consisting principally of iron sulphides, but containing in addition

a small amount of cuprous sulphide. The furnaces used for the treatment of the ores are of two sorts, the one for roasting the sulphides and the other for smelting proper. In both roasting and smelting, however, the purpose is exactly opposite to that existing in the ordinary method of smelting lead ores. Instead of keeping down volatilization of lead, it is encouraged as much as possible.

70. Blowing-Up Furnace.—To accomplish this, both the roasting and the smelting furnaces are of special types,

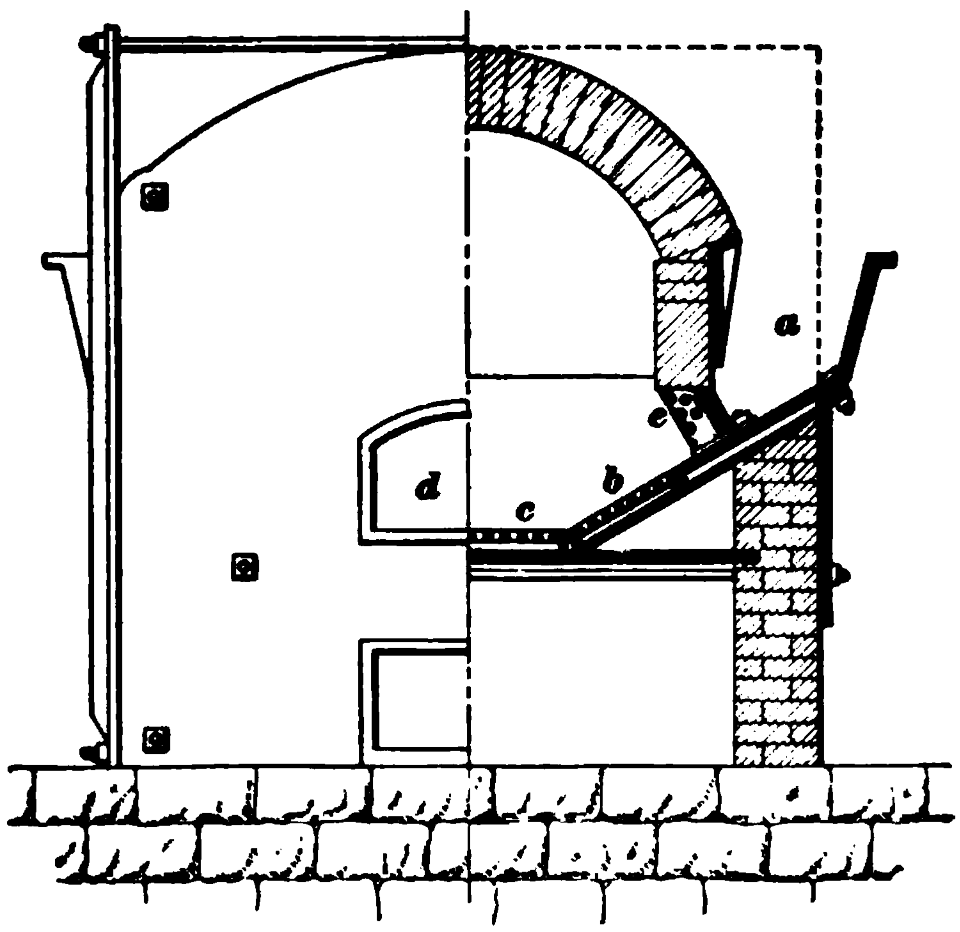


FIG. 21

designed and patented for the purpose. The roasting furnace, or as it is known in this process, the **blowing-up furnace,** is shown in Fig. 21. The ore is crushed and mixed with from 15 to 20 per cent. of slack coal (not coke) and the mixture is charged into the pockets *a*, Fig. 22.

Air is blown into the furnace through the grates at *b* and *c*, and also through the perforated pipes at *e*, Fig. 21. The heat produced is so intense, the lead and zinc are readily volatilized and at once oxidized by the excess of air present, carrying over with them small amounts of sulphur as sulphates, sulphites, and sulphides. As soon as the zinc

has been removed from the ore to a considerable extent, it fuses more or less and is withdrawn from the furnace in a sintered condition. The resulting material, or *cinder*, is

FIG. 22

charged into the blast furnace proper with ores that do not require roasting. If copper is not present, 3 per cent. of copper is added.

71. The blast furnace is constructed of steel water-jackets and is low, as shown in Fig. 23. The feed-hopper *a* is indicated by the man's shovel resting upon it. The slag and matte flow together from spout *b* into the settling pot *c*, from which they flow into the slag pot *d*. The fumes pass from the furnace into flue *e*.

In Fig. 24 is shown a blast furnace with the front removed in order that it may be repaired. The chilled material *b* is also shown in front, on the floor. The rectangular tuyere holes are shown at *a*.

Enough sulphur is left in the roasted ore to form a matte with the copper and iron, and this matte collects most of the gold and silver contained in the ore. The slags run high in silica, 38 to 40 per cent. being the average figure, and contain very little precious metals if sufficient copper has been

FIG. 28

used. The materials that have been carried over with the waste gases from both types of furnace may be divided into two classes: (*a*) Particles carried mechanically; and (*b*) metal that has been actually volatilized and subsequently

oxidized. The gases as they come from the furnaces are mixed and cooled by drawing in a certain amount of air. These pass into a large chamber in which the coarsest particles settle out. From this chamber they pass through a series of flues nearly 1,000 feet in length, where the remainder of the flue dust belonging to the first class is

Fig. 24

recovered almost completely. The gases then enter the bag house, where all material remaining in suspension is filtered out by means of bags of cotton or woolen cloth.

Since the precious metals have been carried mechanically by the draft—not being volatile at the temperature used—it is found that they settle out almost entirely in the system of flues before the bag house is reached, and in this way a fairly complete separation is made between the material that carries

values in precious metals and that which does not. The dust from the flues is returned to the smelting furnace, while the material collected from the bag house is nearly free from silver and gold and is sold for pigment

72. Arrangement of Bag House.—The arrangement of the bag house is as follows: The gases, on entering, are forced in at the top of long cylindrical bags, which are tied at the bottom. The gases make their way through the

FIG. 25

meshes of the cloth, and nearly all the fume that they have carried is thus removed. When much dust has accumulated in the interior of the bags, the current of gas is diverted to a second bag house and the fume is removed by untying the lower end of each bag and giving it a shake over a car, in which the fume is collected. The material thus obtained is taken to the refinery, where it falls through hoppers into iron cylinders, which form in effect the muffle furnace shown in Fig. 25. These are slightly inclined from

feed to discharge openings and are heated to above 800° C. Inside each cylinder a helical iron spiral of the form shown in Fig. 26 is kept revolving from the back end of the furnace. This acts at the same time as a grinder, compressor, and conveyer, and the material is converted by the combined grinding and crushing of this spiral and by the heat of the furnace into material suitable for pigment. As the

Fig. 26

powder falls from the discharge or front end of the cylinder *c*, as shown in Fig. 25, it is conveyed by a screw conveyer *a* to a screen *b*, where any lumps or coarse particles remaining are removed. In composition it is approximately two-thirds zinc and one-third lead; both are present principally in the form of oxides, and the color is nearly a pure white. The principal source of difficulty, as far as the value of the pigment is concerned, is in the occurrence of cadmium in the ores. If this is present, it gives the pigment a decidedly yellowish tinge and lowers its market value.

DESILVERIZATION AND REFINING OF BASE BULLION

73. Cupellation.—The recovery of silver from argentiferous lead by means of cupellation is an extremely old process, having been practiced in times that are almost

prehistoric. Cupellation depends on the fact that oxygen has a much greater affinity for lead than has silver. If a lead-silver alloy is fused and subjected to the influence of atmospheric air at a temperature approaching the melting point of silver, the lead takes up oxygen, forming lead oxide PbO, or litharge, while the silver remains in a metallic condition. This process continues until the lead is entirely oxidized. On account of this property, oxidized substances separate from those in an unoxidized condition, just as water separates from mercury. The litharge rises to the surface and separates cleanly and perfectly from the metal that remains. By removing the litharge as it forms, the lead is separated from the silver, which is left behind.

74. The old method of subjecting all lead containing silver to a process of cupellation was all very well so far as the silver obtained was concerned, but it involved a long period of time, a large consumption of fuel, and left the lead in the form of litharge instead of metallic lead. Devices were sought by means of which the silver and the gold, which always follows the silver in this process, might be concentrated in a small portion of the base bullion, leaving the remainder in a metallic state, free from precious metals and therefore ready for market without further treatment, which would be necessary, in the case of litharge, to reduce it to metallic lead.

The first really successful attempt to accomplish such an end was to concentrate the silver in a portion of the lead through successive recrystallizations; this process is still used to some extent in European desilverization works. The concentration could not by this method be carried beyond a certain practical limit, namely, about 450 ounces of silver to the ton. Later it was found that zinc had the property of forming an alloy with silver, which could be much more readily separated and would result in a much higher concentration of the precious metals. The crystallization process is known as the **Pattinson process** and that in which the zinc is used as the **Parkes process.**

75. The Pattinson Process.—In order to understand the theory on which this process is based, it will be necessary to consider the laws governing the behavior of alloys. An alloy of lead and silver in a fused condition may be considered a solution of silver in lead or lead in silver, according to the metal that predominates, and it is found that these solutions obey, to a certain extent, the laws governing aqueous solutions. Take, for example, a solution of common salt in water.

There is one definite ratio of these two substances that has the lowest freezing point possible to such mixtures; if a solution of any strength be gradually chilled, whichever component is in excess over the quantities required by this ratio will begin to separate—crystals of salt or crystals of ice, as the case may be. As the temperature becomes lower and lower, the ratio of salt and water in the remaining liquid approaches more and more nearly the definite ratio just mentioned. When finally neither ingredient separates, but the solution that has remained liquid solidifies as a whole, it will be found that this definite ratio has been reached and that at the same time the lowest freezing point possible to a solution of salt in water has been obtained.

A solution of silver in lead or lead in silver—a fused mass of lead-silver alloy—acts in a manner exactly similar. There is one definite ratio that has the lowest possible freezing or solidifying point; this ratio is that which exists in lead containing approximately 650 ounces of silver to the ton, which has a fusing point in the neighborhood of 300° C., while that of pure lead is 325° C. Theoretically, then, if an alloy containing silver and lead in any other ratio than 650 ounces of silver per ton be fused and slowly cooled, the metal in excess should separate out until this ratio has been reached, and this is what actually happens; but mechanical conditions enter to such an extent that the metal that separates out carries very considerable proportions of the other metal with it, and it is impossible to continue the action to its theoretical limit.

76. Since there is no reason whatever why base bullion richer than 650 ounces of silver per ton should be reduced in value, the only application of the Pattinson process is made to base bullion containing considerably less than 650 ounces per ton, and the values usually worked upon are from 100 to 200 ounces per ton. In practice the process is carried out as follows:

The base bullion is melted down completely and then allowed to cool gradually. As the temperature falls below the melting point of pure lead, crystals of metal poorer in silver than the original base bullion separate out, leaving the liquid metal richer in silver than the original base bullion. As these crystals form, they are skimmed out by means of a perforated skimmer and set aside. This operation is continued until a certain fixed proportion, usually two-thirds of the metal in the kettle, has been removed. The base bullion has now been divided into two parts, the one richer and the other poorer in silver than the original material. The difference is not very great, but if to each of the parts thus obtained sufficient metal of an equal value in silver, obtained from a similar operation, be added to make up the total amount to a full charge for the kettle, then the process can be repeated. The result will be that these parts will each be divided in two, making four parts in all, carrying varying values in silver.

77. This may be continued indefinitely, and is effected on a commercial scale by using a series of kettles. The number is usually from 9 to 11, but for the sake of simplicity let a case be supposed in which 5 kettles are used and let the value of the base bullion in each of these kettles be assumed as follows: number 1, 3 ounces of silver; number 2, 10 ounces; number 3, 50 ounces; number 4, 150 ounces; number 5, 300 ounces per ton.

Suppose that the base bullion to be treated contains 50 ounces of silver per ton as it comes from the blast furnace. This, then, will be charged into kettle number 3, and upon separation by crystallization, as just described, may

be assumed to give crystals containing 10 ounces silver per ton and a liquid residue containing 150 ounces per ton. (As a matter of fact, no such wide difference in values is ever obtained, and it must be borne in mind that the present illustration has been assumed for the sake of simplicity.) The crystals will, therefore, be removed to kettle number 2, and the liquid lead to kettle number 4. To each of these kettles will be added sufficient metal of the same value, produced by previous operations, to bring the amount in the kettle up to a full charge; kettle number 4 will then be brought to a state of fusion, cooled, and allowed to separate by crystallization. The crystals may be supposed to contain 50 ounces per ton, while the liquid lead remaining contains 300 ounces. The crystals will, therefore, be placed in kettle number 3, while the liquid lead goes to kettle number 5. A repetition of the process in this kettle may be assumed to result in crystals containing 150 ounces of silver per ton, which, therefore, goes to kettle number 4, and liquid lead containing 450 ounces of silver per ton, which is as close an approximation to the theoretical 650 ounces of silver per ton as can be obtained with profit.

78. Now, to consider the metal which has been moving in the opposite direction. The crystals from kettle number 3, containing 10 ounces per ton, are placed in kettle number 2. There, by an exactly parallel method of treatment, these crystals, with an addition from stock on hand of the same value, are divided into two lots, of which the poorer, that is, the crystals containing 3 ounces of silver per ton, go to kettle number 1, while the liquid lead contains 50 ounces per ton and goes to kettle number 3. Crystallization after fusion is then effected in kettle number 1, and results in two products, as before, liquid lead returning to kettle number 2, and crystals, which it may be assumed have been reduced in their silver values to less than 1 ounce per ton. These crystals may then be considered a final product of the process at the opposite end from the enriched base

bullion, and after being cast into bars are ready for sale as market lead.

The process, as thus outlined, is a comparatively simple one, but as a matter of fact the number of kettles is usually much greater, the differences in value in adjacent kettles are correspondingly smaller, and the system becomes decidedly complex. The usual ratio of separation is to take out two-thirds of the contents of the kettles as crystals, leaving one-third behind as liquid lead; sometimes seven-eighths are removed and sometimes a combination of the two. By such a process a considerable proportion of the lead in a form sufficiently free from silver to be marketable without the necessity for cupellation is produced—possibly one-half of the total weight of base bullion treated—while the silver is concentrated in a comparatively small volume of lead, which reduces the amount to be cupeled to a corresponding figure. The plant involved in such a process as described is extensive and the amount of hand labor large.

79. Steam Process.—A modification of this process has been introduced, which is known as the **Luce and Rozan steam process.** It is operated as follows: All the crystallizations are performed in one kettle. This kettle is provided at the bottom with an inlet for steam and an outlet for liquid lead, over which a screen or strainer of perforated iron is placed. When in operation, base bullion is fused in an auxiliary melting pot and then run into the crystallizing kettle by means of a siphon. Through this molten base bullion steam is blown, the kettle meanwhile being covered with a hood to prevent a loss of metal by splashing. The effect of blowing steam through the molten metal is to cool it and at the same time stir it thoroughly; the steam pressure is so adjusted, it will be unable to overcome the increased resistance, two-thirds of the contents of the kettle having become crystallized. The hood is then removed, the outlet at the bottom opened, and the liquid lead allowed to drain from the crystals, which are retained by the strainer. The liquid lead is transferred to one of the auxiliary melting

pots, and the cystals may be charged at once into the second for fusion with a further amount of base bullion of the same tenor, i. e., silver contents, or set aside for treatment at some more convenient time. The operation is then repeated and base bullion of all values is thus separated in the one crystallizing kettle, care being taken, of course, to avoid confusion of lots of different values. The operation is accomplished much more quickly by steam than by hand, and the size of a plant with an equal output is much smaller than in the case of the old method.

80. The Parkes Process.—The Pattinson method was a very decided step in the direction of reducing the amount of lead to be cupeled by concentrating the silver in a comparatively small portion of it, but this has been greatly improved upon by the Parkes process. The fundamental principles on which the Parkes process rests are these: If molten zinc is mixed with molten base bullion, the silver has a greater affinity for the zinc than for the lead, and the result is the formation of a zinc-silver alloy, which is less fusible than the base bullion, very slightly soluble in molten lead, and even less so in lead saturated with zinc. This alloy will separate, therefore, from the molten lead, and, being lighter, will float to the surface in what is known as a crust; in this form it may be skimmed off for subsequent treatment. It is not found practicable to remove all the silver from base bullion of customary grade by one addition of zinc. It would be possible, but the results can be effected much more economically, according to the latest practice, by making the removal in two or at most three operations. Fortunately, zinc has a greater affinity for gold than for silver, so that the gold (which is usually present in variable quantities) is removed very completely and found with the silver in the crust.

The process, however, is by no means as simple as might be judged from the foregoing brief description. The base bullion as received contains impurities in the form of **dross** and **metals** undesirable, as far as the desilverization process

is concerned. Chief among them are antimony and copper, both of which tend to increase the amount of zinc necessary for desilverization, because they combine with zinc either before or during its combination with the silver and therefore not only increase the consumption of zinc, but also increase the weight of the crusts to be subsequently treated. The first step in the process, therefore, is to remove impurities.

81. Softening Base Bullion.—This operation is effected in a reverberatory furnace, shown in Fig. 27, and consists of

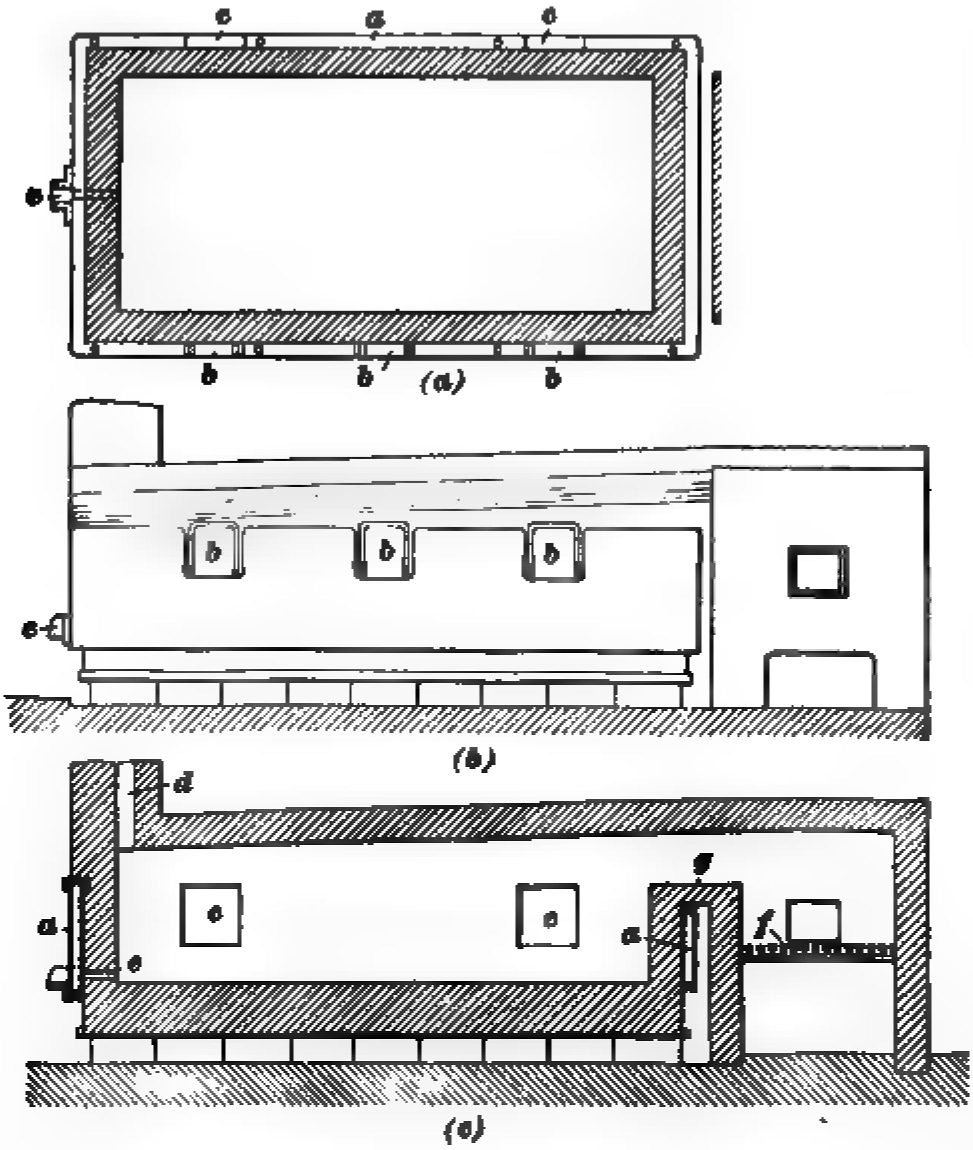


Fig. 27

the following steps: First of all, the base bullion is introduced in bars and is gradually melted down, the aim being

to produce complete fusion at as low a temperature as is consistent with this result. The reason for thus controlling the temperature is that the dross contained is not merely held mechanically; it is to a certain extent soluble in molten lead. The solubility is increased by raising the temperature of the lead. If the operation is properly carried out, the dross rises to the surface of the molten lead in a semi-fused condition and may be removed from the furnace by means of an iron skimmer. This dross, if free from lead, contains principally copper, arsenic, and sulphur, which form speiss and matte when melted down.

The antimony still remains and cannot be separated by purely mechanical means. To remove it, the temperature is gradually raised to a red heat and air is allowed access to the bath of molten metal. Then ensues a process directly comparable to the scorification that goes on in an assay furnace. First of all, metallic lead is oxidized to litharge, and this easily reducible lead oxide yields a part of its oxygen to the antimony, which in its oxidized form unites with the remaining litharge to form what is known as **antimony skimmings.** Any *arsenic* that may have remained after the removal of the dross will probably accompany the antimony. Most of the copper that has remained in the charge, however, will persist until actual desilverization takes place.

82. The amount of antimony in the liquid is determined by means of a test bar of lead, which is poured at intervals, the furnaceman being able to tell by the appearance of the test bar the nearness to the completion of the operation. If such a test bar is taken before any of the antimony is removed and its surface is skimmed just before solidification, by drawing over it a thin piece of wood, it will be found that this skimmed surface, which is therefore free from oxidized products, is dull and gray and in its center a bright crystalline spot will appear, due to the antimony. As the removal of the antimony progresses this spot changes little by little until finally, when the antimony has been entirely removed, the surface of the metal presents a deep blue with fern-like marks of a

crystalline nature, which when more closely examined are seen to be at right angles to one another.

83. Softening Kettles.—Litharge is one of the most corrosive substances that can be handled in a reverberatory furnace, and unless means are taken to protect the hearth, it will be speedily cut through. The firebricks forming the hearth are laid in what is in effect an iron pan *a*, Fig. 27, with double sides. Between the sides water is circulated and by its cooling effect prevents corrosion of the hearth material after a certain point has been reached. Further, by having the entire hearth thus enclosed losses due to possible cutting through at the bottom of the hearth and a consequent leakage of base bullion are prevented.

The furnace is usually constructed of such a size that when its charge has been softened it will be just sufficient to properly fill the desilverization kettles, which at the present time are usually made with a capacity of 30 tons, so that at the beginning of the operation enough base bullion is charged in the softening furnace to yield 30 tons of softened base bullion. The furnace is provided with two sets of doors; on one side are the charging doors *b* and on the other side the skimming doors *c*. The entire hearth is made to slope slightly towards the flue end and directly beneath the flue *d*. At the bottom of the hearth is provided a tap *e* by means of which the molten lead can be withdrawn from the furnace. The arrangement of the plant is usually such that softening furnaces are at such an elevation above the desilverization kettles as to allow the molten lead to flow from the former to the latter by gravity, and ordinarily an iron trough or gutter is used to convey base bullion from the former to the latter. Fire is maintained on the grate *f* and the products of combustion pass over the bridge wall *g*.

84. Zincing.—The base bullion is now in condition for the actual removal of the silver by the addition of zinc. It is run into kettles of hemispherical shape set in brickwork *b*,

Fig. 28, upon which they rest usually by the flange *a*, constructed at the edge. Beneath the kettles a fireplace is situated, and before introducing base bullion from the softening furnaces, the kettles are sufficiently heated so that they will not be cracked or the base bullion chilled. When a full charge has been run in, the first step is the removal of what is known as the **kettle dross**—a comparatively pure litharge, which is returned to the softening furnace. Metallic zinc is then added to the kettle and the whole heated to

FIG 28

such a point that the zinc is completely fused. The zinc used in this "first zincing" is usually the second crust from the desilverization of the kettle, but the net effect is nothing more than an addition of metallic zinc. After the zinc has been fused, the next step is to mix it thoroughly with the base bullion, for it would merely float upon the surface if allowed to remain undisturbed. This process, which was formerly accomplished by hand, is now brought about rapidly and satisfactorily by means of a stirrer, shown in Fig. 29.

The stirrer is in effect a vertical iron cylinder *a* (about 3 feet in diameter for a 30-ton kettle), in which is set a screw propeller *b* in such a position that it causes a stream of molten metal to flow either up or down through the

(c)

(b)

(a)

FIG. 20

cylinder, in accordance with the direction with which it is rotated. Over the whole is placed a hood, or cover *c*, that fits closely to the top of the kettle. Through it projects the shaft *d* of the propeller *b*, which is operated by means of a

small motor *e* placed upon a frame and connected with the shaft by bevel gears *g*, Fig. 29 (*b*). In well-arranged works one stirrer is sufficient to do duty for a series of five or six kettles, being carried from one to the other by a trolley.

When a kettle is ready for the operation of zincing, the stirrer is lowered into position and the propeller started first in one direction and then, after running for several minutes, reversed. In this way a rapid and thorough mixture of base bullion and zinc is effected. When this point has been reached the cover is raised, any adhering crusts removed, and the cover carried to one side, as shown in Fig. 29.

85. Skimmers.—It will now be seen that the kettle contains, floating in the base bullion, masses of unfused material. These are the zinc-silver crusts that carry with them mechanically considerable metallic lead. Their removal is the next step in the process. This was formerly effected by hand, the skimmers working in twos or threes, one man, being provided with a wooden hoe, pushed towards his partners the crusts which they removed with perforated iron skimmers. By having the iron skimmers thoroughly heated before the operation is begun and using care to drain off as much of the mechanically adhering molten lead as possible, the crust may be obtained in a fairly good condition; but even at the best much lead is retained, and under the old system it was necessary to work over the skimmings in a small kettle or furnace, known as the **liquating kettle,** in order that the separation of the lead could be more fully carried out.

86. The Press.—This method has been superseded by the device known as the **press.** The press consists of a shallow, cylindrical receptacle *a*, shown in Fig. 30 (*a*) and (*b*), closed at the bottom by a hinged iron gate *b*, and having a plunger *c* entering the cylinder from above, after the manner of a piston. This plunger is operated by compressed air in the newer types of press.

To operate the press, the bottom is fastened to the cylinder and the plunger raised to give clear working space above the top of the cylinder. The apparatus is then

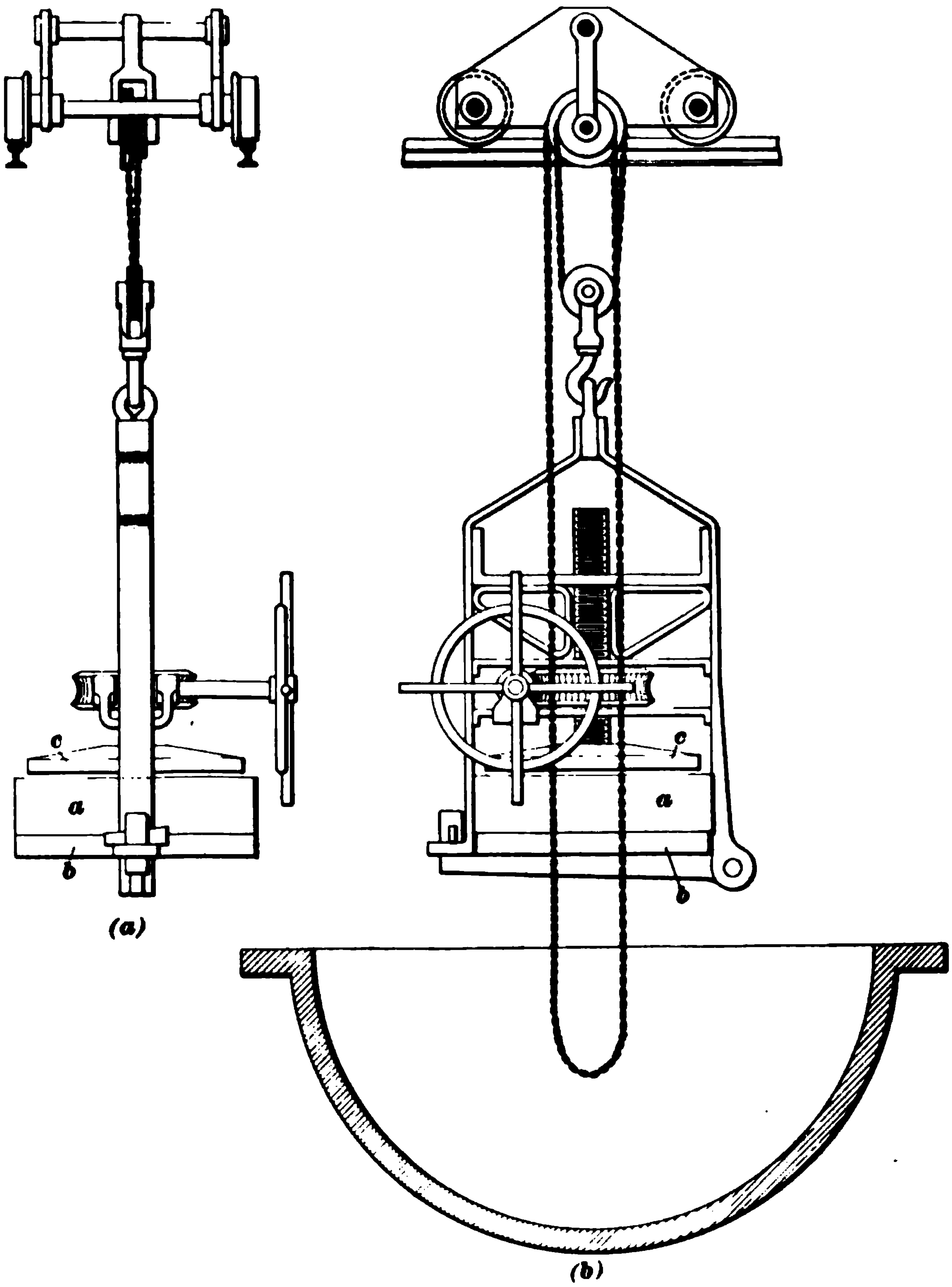


FIG. 30

immersed in the bath of molten metal, so that the top of the cylinder just appears above the surface. The crusts are

then skimmed from the lead by means of the tools described and placed within the cylinder. When this has been completely filled, the press is raised by the same crane used for moving the stirrer and the plunger forced down, thereby squeezing the liquid lead from the crust in a more perfect manner than by the use of liquating kettles. The liquid lead is allowed to drain directly back into the kettle from which the press has been raised. When all has been removed that is practicable, the press is swung clear of the kettle, as shown in Fig. 28, and the hinged bottom dropped, thus allowing the crust to fall out upon the floor. The crust is at once broken up with sledges, a matter easily accomplished at this stage, but difficult when it has had time to cool. The bottom is then raised and fastened again to close the cylinder and the press transferred to the kettle as before.

If the operator of the crane is skilful, by sweeping the nearly submerged press across the surface of the lead in the kettle, he can collect a considerable part of the crust in the cylinder before any is placed in it by hand. The skimming is continued until the crust has been almost entirely removed, when water is sprinkled on the surface of the lead in order to cool it; and the sides of the kettle are scraped to loosen any of the zinc-silver alloy that may have adhered to them. The crust that forms when the lead is cooling is skimmed and pressed, as before. When the temperature of the lead approaches that at which solidification takes place, no further attempt is made to remove the crusts.

87. Second Zincing.—All that has been taken from the kettle up to this point is called the **first crust** and makes up the entire product treated for the recovery of silver. Fire is then started in the fireplace beneath the kettle, the temperature of the metal raised, and a second amount of zinc introduced. The second zincing is carried on exactly as the first, with the exception that the crusts formed are removed directly from the kettle and thrown into a large iron pan without any special attempt being

made to closely separate the lead from the crusts for the following reason:

Suppose that the base bullion at the start contained 300 ounces of silver to the ton. The first crusts removed probably carried with them 90 per cent. of the silver contents, leaving the base bullion in the kettle with, say, 30 ounces of silver per ton. In order to remove this remaining amount of silver, an amount of zinc about equal to the first addition is required, but the crust will only contain 10 per cent. of the silver that was present in the original base bullion. Therefore, although of practically the same bulk, it is only one-ninth as rich as the first crust. This means that in the presence of such an amount of silver as that contained in the original base bullion, the zinc of the second crust is by no means saturated with silver, and, as stated, is added to a kettle of fresh base bullion to serve as the first zinc. This practice effects a saving in zinc and decreases the quantity of crust that it would otherwise be necessary to treat for silver.

88. Assuming the base bullion to have been reduced to 30 ounces of silver per ton by the first zincing, it is aimed to add such an amount of zinc at the second application that the silver contents may be reduced to less than ½ ounce; in some works $\frac{2}{10}$ ounce is the maximum allowed in the desilverization of lead. With experience, it is possible to come within the limit named four times out of five.

If the silver contents run higher than the limit, a slight addition of zinc is made and another crust taken off, which is added to the second crust. This practice is much in advance of the methods formerly used, where four or five crusts were necessary to remove the silver and each crust was kept separate and required treatment in the liquating kettle. The amount of zinc added at each of the two steps described is in the neighborhood of 1½ to 2 per cent. of the total weight of the base bullion, but since the second crust serves as the first zinc, this means that each zinc charge is used twice and that, therefore, in most cases but one charge of fresh zinc to

a kettle is necessary. Elaborate tables designed to indicate the amount of zinc required to reduce base bullion to any given silver contents have been calculated. In most works, however, the necessary information is gained from experience.

89. Concentrating Gold by Zinc.—The gold contents of the base bullion, with whatever copper may be retained after its treatment in the softening furnace, are taken up by the zinc before the silver and in preference to it. On account of this affinity for gold and copper, if a very small amount of zinc be added at first, little more than sufficient to combine with such gold and copper as are present, the gold and, incidentally, the copper may be concentrated in one small crust, carrying with it a certain amount of silver. This method was formerly practiced, but it involved an increase in the number of crusts that required separate treatment if anything was to be gained; and since the product of the cupels contained both gold and silver, the bullion required parting in any event, so that the production of the **gold crust**, as it was called, has been abandoned and the gold and silver concentrated together in one crust.

90. Removal of Zinc.—After the removal of the second crust (or the third, if such had been found necessary) the lead is practically free from silver, but contains in solution a small amount of zinc. The solubility of zinc in lead depends on the temperature of the lead, but even when reduced to nearly the solidifying point almost 1 per cent. of zinc will be retained, and this must be removed before the lead is ready for the market; otherwise it will be hard, subject to attack by sulphuric acid, and unsuitable for use in the manufacture of white lead. The next step, therefore, is to remove this zinc together with any minute portions of other metallic impurities that may have survived the previous treatments. To accomplish this, the lead is transferred by means of a siphon, constructed of iron pipe, to the refining furnace or kettle, as the case may be.

The removal of the zinc depends on the fact that zinc has a higher affinity for oxygen than has lead. The oxygen may be supplied by the introduction of steam or by a process almost exactly parallel with the softening of base bullion.

FIG. 31

91. If the latter method is adopted, the refining furnaces are almost the counterparts of the softening furnaces, except that they may be slightly smaller since the amount of

material treated at a charge has been somewhat reduced. The chemical action is again closely allied to scorification; that is, the lead is first oxidized and then, in turn, gives up part of its oxygen to the zinc, forming a slag-like material composed of a compound of zinc and lead oxides. This is removed by skimming, and by frequently making test ingots the complete removal of the zinc is finally determined. The removal of the zinc goes on only at a bright red heat and it cannot be allowed to fall below this point during the process.

If the desilverized lead is to be refined by steam, an iron kettle *a* is used, as shown in Fig. 31. Then the lead is heated to a bright red and steam is introduced by means of a bent iron pipe *b*. The kettle is covered during the operation by a hood *c*, similar to that in use for the Pattinson steam process. At the temperature used, zinc has the power of decomposing water and taking its oxygen from it. This results in the formation of zinc oxide and a small amount of lead oxide; both rise to the surface of the kettle in the form of a yellowish powder. When the operation has been completed, the hood is removed and the powdered material skimmed from the surface. The kettle may be the one in which desilverization took place or a separate kettle may be used, as may seem best, for its use for refining lead shortens its life materially.

92. Casting the Lead.— In whatever manner the removal of the zinc has been performed, the next step is to cast the refined lead into pigs. If the refining was done in a reverberatory furnace, the lead should preferably be removed to a kettle in which it can be brought to exactly the right temperature for casting. Casting direct from the reverberatory will tie up that furnace for too long a time and will cool it down far below the point at which refining takes place. It will then have to be heated up for the next charge and a further amount of time be lost.

If the refining has been done by steam, it is also advisable to remove the lead to a kettle kept especially for the purpose, although in this case it is possible to accomplish

desilverization, refining, and casting with only one kettle. The casting itself is conveniently accomplished by means of the siphon constructed of iron pipe *a*, shown in Fig. 32. The molds *b* are arranged in a semicircle below the kettle; the siphon is plugged and filled with molten lead while in an inverted position, then put in the position shown, and opened when the flow of lead will begin. The longer limb of the siphon terminates in a swinging arm, whose length is equal to the radius of the semicircle in which the molds have been

FIG. 32

arranged. Without checking the flow of molten lead at any time, the molds are filled in succession and each one is skimmed as soon as filled by the molder, who removes any dross or dirt from the surface by means of two pieces of shingle. In this way clean pigs of lead are produced, and the whole operation can be easily managed by one man who skims the lead in one mold while the next is being filled from the siphon. Before the last of the molds in the semicircle has been filled, that which was first cast has solidified and

has been cooled by water thrown on from a hose; the pigs of lead are removed as fast as cooled, and when the end of the semicircle has been reached the first molds are again ready to be filled, so that the operation may be carried on without noticeable interruption. Dip samples are taken for assay, as in the case of casting base bullion in a similar manner.

93. Treatment of Crusts.—The average weight of the crusts obtained by desilverization of the base bullion is usually less than 10 per cent. of the total weight treated. Practically all the silver from a 30-ton charge of base bullion containing 300 ounces of silver to the ton is contained in the crust, which will have a value ranging from 3,000 to 4,000 ounces of silver per ton of crust. In addition to the silver, gold, and copper that are present in very small amounts, the crusts contain from 12½ to 15 per cent. of zinc, the balance being lead.

94. The Recovery of Zinc and Silver From Crusts. Two methods have been in use for converting crusts into material that could be profitably treated by cupellation. One, which involves smelting the crusts in a small blast furnace, destroys the zinc entirely, since it reappears in an oxidized condition in the form of slag, from which it may not be recovered. The second method of distillation recovers a large part of the zinc, say two-thirds of the total amount used, and leaves the rich base bullion in proper condition for cupellation.

This method, which has been almost universally adopted, depends on the fact that metallic zinc is volatilized at a temperature slightly below 1,000° C., also that zinc can be distilled in such a way as to recover a large proportion of it. After such distillation, the lead and silver are found as a residue and are in condition for cupellation.

95. The distillation of zinc from the crusts is accomplished in retort furnaces usually of the type known as the *Faber du Faur*, which are shown in Figs. 33, 34, and 35.

As will be noted from the illustrations, the furnaces are in essential particulars hollow cubes of firebrick bound with

iron, provided at the bottom with grate bars *b*, as shown in Fig. 35, or in case oil is used as a fuel, some one of the various types of oil burners. These cubes are supported by trunnions *c* upon a frame *d* in such a manner that they may be tilted by means of the differential pulley shown at *c*, Figs. 33 and 34. A retort *f* of graphite and fireclay is enclosed within the furnace in an inclined position and supported by firebricks *g*, Fig. 35 (*a*). The mouth of the retort protrudes from the front of the furnace and the incline is such that

FIG. [illegible]

by rotating the entire apparatus through an arc of from 30° to 45° the molten contents may be poured from the retort into molds *a*, Fig. 34. Heat is supplied by bituminous coal charged from above, or by fuel oil, as the case may be.

In operating, a charge of broken zinc crust is placed within the retort when it is in a normal position, as shown in Fig. 35, and also a small amount of pulverized charcoal, in order to prevent as far as possible oxidation of the metallic zinc. Over the mouth of the retort, a condenser *b*, mounted on a truck *c*,

is luted on with plastic fireclay, as shown in Fig. 33, in such a manner as to exclude the air as perfectly as possible. The condenser has two outlets; the upper one is opened at times to note the progress of the operation, while the lower one is kept closed until such time as it is desired to tap out the molten zinc that has accumulated.

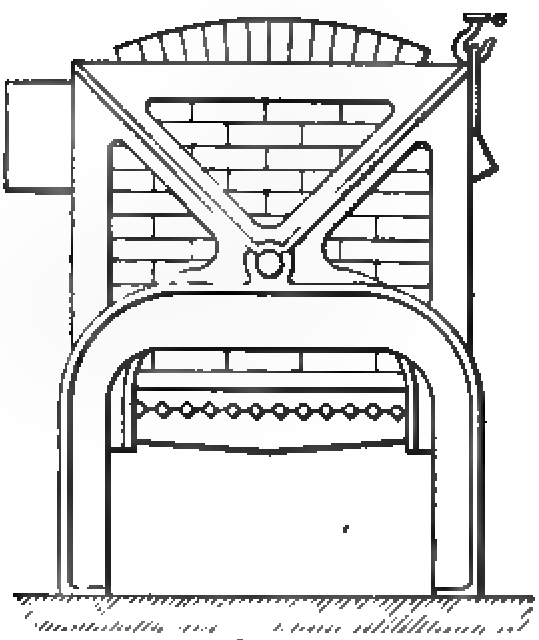
Heating is begun, and when the temperature has been raised to the boiling point of zinc, vapors of the metal begin

FIG. 34

to come over into the condenser and make their appearance at the vent hole, burning with the characteristic zinc flame, accompanied by the copious white fumes of zinc oxide, produced by the combustion of the metallic zinc. Distillation is continued until all zinc that it is practicable to remove in this way has been driven off. This stage is indicated by the appearance of a yellowish color in the fumes from the vent hole, caused by the commencement of the imperfect distillation of lead and the formation of lead oxide.

The molten zinc in the condenser should not be tapped out until the operation has been completed, because the zinc

is extremely difficult to condense in such a way as to yield a liquid or solid product. The tendency is to form a powder, known technically as **blue powder,** which is not available for processes of desilverization. By keeping in the condenser a certain amount of liquid zinc to serve as a nucleus



(c)

FIG. 35

for the condensation, the blue powder formation is reduced in bulk.

96. At the conclusion of the operation, which is indicated by the appearance of lead oxide, the molten zinc is

tapped out from the condenser into a mold *h*. The condenser is next removed from the retort by breaking the luting and pulling back the carriage. The molten residue, consisting of lead and silver with perhaps 1 per cent. of zinc, is poured from the retort by tilting the furnace to such a position that the metal can flow into a mold placed to receive it. A fresh charge of zinc crust is then introduced and the operation is repeated.

In a furnace of ordinary size, such that 1,000 pounds of crust may be treated at a charge, it is customary to treat three charges per day of 24 hours. The zinc, which may contain a certain amount of silver that has been mechanically carried into the condenser, is immediately utilized in further desilverization operations, so that the silver is not lost. In order to recover any possible losses of the greatly enriched base bullion, due to leakage of the retort or the spilling of the metal, the ashes and all sweepings from about the retorting furnaces are smelted in the base-bullion blast furnace.

The silver has now been concentrated in so small a quantity of lead that it forms usually about 10 per cent. of the total weight, and no further condensation has been found to be commercially possible up to the present time without cupellation, involving the removal of the lead in the form of oxide.

97. Treatment of By-Products.—In the process of refining and desilverization, a number of by-products have been formed, which contain materials of value; these should be recovered in order to reduce the cost of the operation as far as possible. The principal ones are the dross removed in the softening furnace, the softening skimmings, or *antimony skimmings*, as they are called, and the refining skimmings.

The **dross**, which is the first to be obtained, contains considerable copper, as well as lead in a free and combined state. It is treated in the reverberatory furnace, where the lead is separated from the remaining substances as far as possible. This is returned to the softening furnace with

the next charge, while the dry dross remaining is charged into a blast furnace, when it is to be used for the resmelting of roasted matte.

98. The **antimony skimmings** are also treated in the reverberatory furnace. They are melted down and the flame is made smoky and reducing in chemical action, the purpose being to reduce a small amount of the lead that was oxidized in the softening furnace. The softening skimmings contain a certain amount of silver, less, it is true, than the base bullion from which they were produced, but still an appreciable quantity. By reducing a small portion of lead it acts as a collecting agent and carries with it to the bottom the greater part of the silver present. This fusion also affords an opportunity for the lead that has been mechanically carried in the skimmings to settle out and be withdrawn from the hearth of the furnace by means of a tap on one side and returned to the softening furnace.

The **liquid skimmings,** as they are called, are drawn out through a tap at a higher level on the opposite side of the furnace. These now consist of lead and antimony in an oxidized condition and are charged into a small blast furnace, usually circular in cross-section, and smelted for hard or antimonial lead.

The **refining skimmings** are likewise liquated in the reverberatory and the metallic lead recovered with the desilverized lead, which is to be refined, while the skimmings themselves, after liquation, are smelted in an ordinary blast furnace. It is found that in spite of the action of the softening furnace in removing antimony, a certain amount almost always follows the lead and is only removed in the refining furnace.

CUPELLATION

99. Cupellation, as practiced in the commercial recovery of silver, is different in many respects to that which is carried out in the assay furnace. In the assay furnace the oxidized lead is removed by volatilization in a current of air

or by the absorption of the cupel material. On a commercial scale, both of these actions go on to a limited extent only. The lead oxide is principally removed as litharge, which is allowed to flow from the cupel, or **test,** as it is technically known.

Two principal methods of cupellation are in use, the German and the English. The German method is utilized on the Continent and in Europe, while the English method is followed in this country. Without taking the German method up in detail, an enumeration of its salient points are given.

100. German Method of Cupellation.—Reverberatory furnaces, with movable roofs and stationary hearths, are the type in which the oxidation of lead is effected. The hearth is usually circular in form and is constructed of a mixture of limestone and fireclay in most cases; it is supported at its foundation by an iron plate in order to prevent any serious leakage of silver into the foundations. The furnace is constructed of such a size as to receive a full charge at one time, in modern works usually in the neighborhood of 25 tons. The enriched bullion most frequently used in such a furnace, however, is usually that resulting from the Pattinson process, and is consequently lower in silver than that produced by the Parkes process.

The charge is introduced before the roof is put in place and is brought to a state of fusion. Air at a pressure of 8 ounces is then blown across the surface of the molten lead in the direction of the working door and results in the formation of litharge. This is allowed to flow from the furnace in a practically continuous stream, which is regulated by cutting a gutter through the hearth material at the working door. By cutting the gutter lower and lower, the removal of the litharge is continued as the level of the molten metal in the cupeling furnace falls.

The removal of the litharge is so regulated that it forms a ring about the edges of the bath of molten metal, leaving the metallic contents of the hearth exposed at the center in

just the same manner as will be noted in running a scorification assay in the muffle furnace when the slag has begun to form well.

101. This regulation of the removal of litharge is a matter requiring careful watching. If it is effected too rapidly, there is danger that silver will be carried away by it, and in order to avoid this, sufficient time should be allowed to permit the silver thus held to be reabsorbed by the bath of lead over which it must move in order to reach the outlet. On the other hand, if the litharge is removed too slowly, oxidation is hindered and the process very much lengthened. The removal of the litharge is continued until all the lead has been entirely eliminated.

The hearth has been provided during its construction with a slight hollow sufficient to hold the amount of silver resulting from a charge and in which the **brightening** takes place. Firing is at once stopped and the furnace cooled off. As soon as it is possible, a stream of water is directed on the silver in the hearth, which is thoroughly chilled. It is then taken out in a solid mass, the roof of the furnace having been previously removed and the upper layer of the hearth torn up to recover any silver that may have penetrated into it. The crude silver thus obtained in a cake is purified or refined by fusing in a graphite crucible and adding silver sulphates; this decomposes, forming sulphates of the base metals present and metallic silver.

102. English Method of Cupellation.—In the English method, which is the one in use in this country, a much smaller furnace is employed, the capacity being little more than 1 ton, as a rule. The construction is just the reverse of that of the German furnace, the roof and sides being stationary while the hearth itself is movable. Fig. 36 shows the arrangement. The fireplace *f* is at one side of the hearth and the flue *g* at the other. The blast is introduced from the back at *b* and goes towards the working door, which is in the front.

Another point of essential difference from the German furnace is in the method of working. In the English method rich base bullion is introduced to the furnace from time to time in order to take up the room that has been left vacant by the removal of lead through oxidation; that is, the process is to a certain extent a continuous one, lead flowing out at the front *c* in the oxidized form as litharge, while argentiferous lead in the metallic form is introduced at or near the back.

FIG. 36

The hearth of the furnace is the feature to which especial attention is called. As stated, it is movable and enclosed in what is called the test ring *a*. This has a frame, usually oval, but sometimes rectangular, of wrought or cast iron, into which the hearth material is packed.

As stated in the general outline of the purposes of cupellation, it is not desirable to construct the hearth of a material that will absorb litharge to any extent, since the removal of the litharge is accomplished by allowing it to flow out. Originally the hearth was constructed of a mixture of limestone and fireclay, as in the case of the German furnace, but it has been found that Portland cement makes

a better and more durable hearth and the tests in the most modern works are built with the latter material. In order to overcome the corrosive effect of the litharge at the level of contact between lead and air, an iron pipe bent to the proper shape is embedded in the hearth material, so that it will encircle the cavity containing the metal at this level as nearly as possible.

In preparing a test for use, it is filled with plastic cement flush with the sides. The cement is rammed in place and after completely filling in this manner, the hollow to contain the metal is cut in by means of trowels. In this way a more uniform hardness is obtained than if the hollow were formed in the process of building up the hearth. When the filling of the test ring has been completed and the material is thoroughly dried, the carriage *d* upon which the test ring is mounted is run underneath the stationary portion of the furnace and the test ring lifted into close contact with it by means of the jack-screws *e*, or whatever device may be provided for the purpose.

103. The Process.—A sufficient amount of enriched base bullion from the retorts used for the removal of the zinc is then introduced and cupellation is begun. This operation is continued until the contents of the hearth run from 50 to 70 per cent. silver; then one of two methods may be adopted: Either all of the furnaces in the series, except one, are used for bringing the enriched base bullion up to this standard, that is, 50 to 70 per cent. silver, and then the finishing or refining is done in one furnace; or the furnaces are worked in pairs and then used alternately as finishing furnaces. When 50 per cent. base bullion has been produced, the contents of one furnace are added to those of the one that, in this case, has become the finishing furnace. By the former method it is possible to employ a rather inferior grade of labor at all of the furnaces, except the one in use for finishing.

When the lead has disappeared the silver is technically said to have brightened, but the stage is not nearly so well

marked as is the brightening of the silver obtained on an assay cupel. Usually the silver is next refined by further heating with the addition of niter, which acts as an oxidizing agent upon whatever base metals there are still in the bath. After refining, the silver is ladled from the hearth and cast into bars, which, if they are to be parted by electrolysis, are of the shape required for the anode.

It is to be understood that the small percentage of gold that is almost always present in this operation follows the silver and acts in a manner exactly corresponding; that is, the silver-gold alloy, or **doré** bullion, as it is technically known, acts precisely in the same manner as silver alone. In the cupeling room, as in the retort room, all refuse is sent direct to the base-bullion blast furnace to recover the silver values that it may contain.

104. The English method of cupeling is much more rapid than the German, on account of the great loss of time involved in reconstructing the hearth of the German furnace for every charge. When the hearth of an English furnace gives out, it is only a question of replacing it with a fresh one that has already been prepared—a matter of minutes instead of days. The litharge produced by the English method is much richer in silver than that produced by the German, since lead is being constantly added to metal containing an increasing percentage of silver, and the amount of silver carried by the litharge is dependent on the percentage of silver in the metal being cupeled; but since the litharge can all be resmelted and is in fact desirable for that purpose, the actual loss involved at this point is more apparent than real.

PARTING

105. Parting With Acids.—The bullion produced by cupellation is almost always a mixture of silver and gold, with small but varying amounts of base metals, the principal one, and in fact the only one worth noting, being copper. The purity of the bullion is denoted by parts in 1,000, that is,

instead of saying a bullion is 99 per cent. pure, it is said to be 990 fine, meaning that 990 parts out of 1,000 are precious metal and 10 parts impurities.

The separation of the gold and silver becomes the next step in the production of bullion for the market. This operation is called **parting** and is accomplished in one of two ways. Either the doré bullion is immersed in nitric or sulphuric acid, which attacks the silver, but leaves the gold untouched, or it is separated by electrolysis, the silver being deposited from an electrolyte of silver nitrate $AgNO_3$ and dilute nitric acid. In this case also the gold is unaffected and drops to the bottom as mud or slime.

In parting by acid, it is found that if the doré bullion contains more than a certain proportion of silver, the acid will dissolve out the silver effectually. According to some authorities, this proportion is as low as two parts of silver to one of gold; according to others, more silver must be present. If gold is in excess, the acid is unable to remove the silver. If the parting is to be effected by nitric acid, no serious impediment is offered by the presence of copper in the doré bullion; with sulphuric acid, however, if the copper is in excess of 10 per cent. anhydrous copper sulphate is formed, which is insoluble in concentrated sulphuric acid and coats the metal to such an extent that further action is stopped.

106. In parting by nitric acid, the granulated bullion is boiled with strong acid in vessels that must be of either porcelain or platinum. After the silver has been entirely dissolved, the solution is drawn off by decantation and the gold residue washed thoroughly, first by boiling with a fresh amount of nitric acid, which is added to the acid used for dissolving the next doré bullion, and then by successive additions of water. From this solution of silver nitrate the silver is precipitated by means of common salt as silver chloride $AgCl$, and after washing, granulated zinc is added, which reduces the silver chloride to metallic silver, zinc chloride $ZnCl_2$ being produced by the exchange. The zinc chloride is removed from the mass of precipitated silver,

known as cement silver, by a further thorough washing with water, and the cement silver is then fused in graphite crucibles. Wash waters are run through filter presses in order to recover any values which may otherwise escape.

Formerly nitric acid was the only acid used for parting operations, but it had the disadvantage of being expensive, since it was necessary to dissolve the silver in either porcelain or platinum vessels. It was afterwards found that sulphuric acid acted quite as efficiently in separating silver and gold, and at the present time practically all acid parting is brought about through the use of this acid. Aside from its much lower cost, the great advantage in the process is that iron kettles can be used, since sulphuric acid stronger than 66° B. does not attack metallic iron, while boiling acid of that strength dissolves silver readily.

107. Cement Silver.—The doré bullion is treated in a manner quite parallel with that employed when nitric acid is used until the silver has been dissolved. At this point, however, it is necessary to change the process, since silver sulphate is only slightly soluble in dilute sulphuric acid or water. The solution is drawn off and one of two methods may be followed. Either it is boiled and diluted by the introduction of live steam, in order to prevent precipitation, or water is added with the direct purpose of causing the precipitation of silver sulphate, which can then be removed from the cool diluted acid. Metallic silver is recovered from the silver sulphate in the former instance by suspending copper plates in the boiling solution. The copper replaces the silver, forming copper sulphate, while cement silver is thrown down. If the silver sulphate has been precipitated, it is mixed with sheet iron in such proportion as to reduce all of the silver, but none of the copper, which may be present. In this case ferrous sulphate is formed and metallic silver, as in the former instance. By whichever process it has been obtained, the cement silver is then washed thoroughly with water until no traces of sulphuric acid or copper appear in the wash water, after which it is put into a filter press

between cloths and pressed into cakes. These cakes are then melted down in graphite crucibles with a little niter, as previously described.

Fig. 37

The gold is purified by boiling with further amounts of sulphuric acid from five to seven times, in order to completely remove the silver. It is then washed and dried and the resulting powder fused in crucibles.

In some parting works, washing with water is an intermediate step between two or more of the boilings with acid. In Fig. 37 is shown the upper part of the parting kettle. The hood doors *a* can be removed by the handles. The stack *b* carries off the fumes to the fume box *c*. The acid tank shown at *d* is connected with the parting kettle by means of the pipe *e* through which the acid flows.

SPECIAL PRACTICE IN SOUTHEASTERN MISSOURI

108. The ore in southeastern Missouri consists of grains of non-argentiferous galena disseminated through a gangue of dolomitic limestone averaging, perhaps, 7 per cent. of lead before concentration. This is concentrated to a product containing from 55 to 75 per cent. of lead and a small part of it is smelted in reverberatory furnaces of the Flintshear type. A larger part, however, is smelted in small blast furnaces of a special form, which are worthy of note. The ore is roasted in hand reverberatories to a low percentage in sulphur and then charged with puddle cinder or roasted matte as flux into the round blast furnace, with about 12 per cent. of coke as a fuel. The height of the blast furnace is, say, 10½ feet from the tuyere level to the feed opening and its diameter is 56 inches at the feed opening and 40 inches at tuyeres. Very low blast pressure is used, running usually from 8 to 16 ounces. The slag made contains about 33 per cent. of silica, 38 per cent of iron, and the remainder lime, magnesia, and impurities. The lead produced is rather impure from a chemical standpoint, which, however, is no drawback for the purposes the lead is intended, and after remelting it is cast into pigs and sold under the name of chemically hard lead, to be drawn into pipe for special purposes. On account of its impurities, it takes a bright silvery appearance when drawn into pipe and retains this much longer than ordinary pure lead.

ZINC SMELTING AND REFINING

PROPERTIES OF ZINC

1. Physical Properties.—Zinc is a white metal with a bluish tinge, crystallizing in the isometric system into grains or plates, according to the temperature at which it is cast. The luster of the crystals is bright on a fresh surface. The specific gravity is about 7.4. Different authorities vary widely upon the point of specific gravity, but this is undoubtedly due to the fact that it can be changed greatly by variations in the treatment given it; for example, after rolling, it may be found to have raised from 7.2 to 7.4. Zinc is not ductile below 100° C.* or above 200° C. Between 100° and 150° C. it is ductile and malleable and may be rolled into plates. Its melting point when pure is 433° C., and at a temperature of about 920° C. it boils and may be distilled without further difficulty. The metallurgy of zinc on a commercial scale depends at present entirely on this important fact. The condensation of zinc vapor is a matter requiring great care, for if diluted with even inert gases, like nitrogen, it becomes more and more difficult to condense in a solid form, and finally, if the dilution be carried too far, nothing but a powder is produced. The temperature of

* To change Centigrade into Fahrenheit, divide by 5, multiply the quotient by 9, and to the product add 32; thus, $100° C = \frac{100 \times 9}{5} + 32 = 212°$ F.

condensation is also a matter of importance, and it is stated that only effective condensation takes place between 415° and 550° C. If the vapor as formed be allowed to come in contact with air, it burns with a characteristic greenish-white flame, dazzlingly bright, producing great volumes of white zinc-oxide fumes.

2. Zinc alloys with a number of metals, the most important being copper, forming brass. It may also contain a number of metals as impurities. Of these, however, only three are of sufficient frequence and effectiveness to be worthy of note—namely, cadmium, iron, and lead. **Cadmium** is a very frequent impurity, because on account of its closely allied nature to zinc; cadmium ores are nearly always found with zinc ores. It hardens zinc somewhat, but since it is found in very small quantities, as a rule, its effects are rarely injurious. Iron is also frequently present, and it may be retained in considerable quantities, but is usually removed by a process of refining before zinc is put on the market. If present to an extent greater than 1 per cent., it interferes with the properties by virtue of which zinc may be rolled into sheets, and is also injurious in zinc that is to be utilized for the desilverization of lead. **Galena,** or sulphide of lead, is frequently associated with zinc ores, and the two metals are extremely difficult to separate; in fact, no process for their complete separation has been put in successful operation. The amount of zinc that can be held in solution by lead increases with the temperature of the molten lead; the percentage of lead retained by molten zinc varies in exactly the same manner. Lead is removed from zinc by a process of refining before being marketed. In general, its effect is to make zinc tender.

3. Chemical Properties.—Although zinc stands high in the scale of metals as arranged with respect to their electropositive or negative qualities—that is, nearer to the alkali-metals end of the scale than copper or iron, for instance—it is not readily oxidized by air or water at ordinary

temperatures. In the presence of carbon dioxide CO_2, water, and watery vapor, it becomes coated with basic carbonate of zinc, which protects it from further change. Upon heating in air or in a current of steam, the power to take up oxygen becomes much greater.* As has been seen, zinc vapor burns very readily, and it is even possible to burn the metal before volatilization takes place. Zinc is attacked by most acids, although when pure it is less readily attacked than when impure, due probably to the fact that its solution by acids causes the evolution of hydrogen, which acts as a protective film if the zinc be pure, while if impure, an electric couple is formed between the zinc and the metal forming the impurity, and on account of the electropositive quality of zinc, the impurities almost invariably constitute the negative pole and the hydrogen is consequently liberated at that pole. Zinc is also soluble in solutions of caustic alkalies and water, and some types of electric cells are made dependent on this property. Heated in contact with carbon monoxide CO, no action takes place. Heated in contact with carbon dioxide CO_2, zinc is partially converted into zinc oxide ZnO, with a corresponding partial decomposition of the dioxide into carbon monoxide and the oxygen necessary to form the oxide of zinc. In this instance, also, as in the case of the decomposition of water, an equilibrium is reached, depending on the relative amounts of the various compounds present and on the temperature at which the action occurs.

4. Compounds of Zinc.—Of the many compounds which zinc may form, but four are of importance in connection with its metallurgy, as thus far developed: Zinc oxide ZnO, zinc sulphide ZnS, zinc silicate Zn_2SiO_4, and zinc sulphate $ZnSO_4$. The carbonate $ZnCO_3$, which occurs as a mineral, is readily decomposed by heat into zinc oxide ZnO and carbon dioxide CO_2, and which, for all the purposes of metallurgy, may be considered as equivalent to zinc oxide.

* At red heat steam is decomposed in part.

TABLE I

SOLUBILITY OF LEAD AND ZINC AT VARIOUS TEMPERATURES

(Spring and Romanoff.)

Temperature C°	Lower Stratum		Upper Stratum	
	% *Pb*	% *Zn*	% *Pb*	% *Zn*
334	98.8	1.2	....	....
419	....	....	1.5	98.5
450	92.0	8.0	....	....
475	91.0	9.0	2.0	98.0
514	89.0	11.0	3.0	97.0
584	86.0	14.0	5.0	95.0
650	83.0	17.0	7.0	93.0
740	79.0	21.0	10.0	90.0
800	75.0	25.0	14.0	86.0
900	59.0	41.0	25.5	74.5

The above table shows that the saturation point of lead-zinc alloys increases with the temperature. At a point 2° or 3° C. above the melting point of zinc, the latter still retains 1.5 per cent. *Pb*. In refining lead-bearing zinc by gravity, it is impracticable to go below that point.

5. Zinc oxide occurs in nature as **zincite,** a red mineral. When produced by burning zinc vapor, it is white and is largely used as a pigment under the name of **zinc white.** It is infusible and only volatile at high temperatures. It is easily reduced to a metallic form by carbon at a bright-red heat, and most of the zinc produced is obtained as a result of this interaction. When heated in the presence of either carbon monoxide or hydrogen, as has already been intimated, a state of equilibrium is attained. A certain amount of zinc oxide is reduced by a corresponding proportion of carbon

monoxide or of hydrogen, as the case may be, resulting in the formation of carbon dioxide or water, respectively. When the more highly oxidized forms bear a certain ratio to the reducing agent or gases, it would seem that a chemical equilibrium is established and no further action takes place in either direction. This ratio is a function of the temperature and is not capable of definite determination. Apparently, the higher the temperature, the greater the oxidizing effect of either carbon dioxide or water. This would seem to be especially probable in the case of carbon dioxide, which is known to be dissociated at high temperatures into carbon monoxide and oxygen; the logical inference is that the affinity for the second atom of oxygen decreases with their increase of temperature.

6. Zinc sulphide is the form in which by far the greater part of zinc occurs in nature and is known as **black jack, blende,** and **sphalerite.** This substance is almost infusible, and if volatile at all, is so only at very high temperatures. When heated in the air, it is oxidized with the formation of zinc oxide and zinc sulphate and the evolution of sulphur dioxide SO_2. No effective method of reducing zinc sulphide directly to metallic zinc (which at least is capable of being utilized upon a commercial scale) is known, and therefore zinc sulphides which are to be used as a source of metallic zinc require proper roasting into oxides.

7. Zinc silicate occurs in nature as **willemite, calamine,** or **electric calamine.** It is also formed when zinc oxide and silica are heated to a white heat, but this action is not of importance in connection with its metallurgy. When heated to a high temperature, zinc silicate is completely reduced by carbon, with the formation of metallic zinc, carbon monoxide, and silica slag. It is, therefore, possible to produce the metal from silica ores without previous separation. To the compounds already mentioned, as the zinc ores of importance, should be added zinc carbonate $ZnCO_3$, known as **smithsonite.** This latter compound is readily

decomposed upon heating with the formation of oxide and needs no further consideration.

8. Zinc sulphate is decomposed at a yellow heat into zinc oxide with the evolution of sulphur trioxide SO_3, sulphur dioxide SO_2, and oxygen. This is the action aimed at in the roasting process, and on account of the fact that it is extremely imperfect at any except high temperatures, the satisfactory roasting of zinc-sulphide ores is a matter of considerable difficulty. Zinc sulphate is decomposed by carbon at a red heat into zinc sulphide and carbon monoxide, attended by a slight evolution of SO_2 and a corresponding formation of metallic zinc. The production of metallic zinc in this manner is both small and uncertain, and the principal effect is merely the reduction of sulphate to sulphide, in which form no further action of the carbon takes place. This fact is to be borne in mind with reference to the necessity for as close a removal as possible of sulphur in the process of zinc roasting. On account of its ready solubility in water, zinc sulphate is of rare occurrence in nature.

TREATMENT OF ZINC-LEAD SULPHIDES

9. The Zinc-Lead Sulphide Problem.—One of the most vexing problems that confronts the metallurgist today is the treatment of mixed sulphides of zinc and lead. There are enormous quantities of blende and galena in the United States, which at present are not valuable because of the impossibility of treating them at a profit. The problem of their treatment embraces both the physical and the chemical characteristics of the metals in these ores. Lead and zinc do not alloy to any appreciable extent, but each absorbs just enough of the other to make the metals impure.

If zinc ore is treated in a blast furnace, the zinc will volatilize and then condense in the throat of the furnace, forming

a hard infusible lump, which will in time close the throat or cause frequent stoppages in order to clean it out. The great heat that occurs in the lower part of the furnace causes a loss by volatilization. On the other hand, if the ore is smelted for zinc, the lead forms a fusible compound with the silicious materials present and prevents any successful recovery. Many attempts have been made to master the problem of successfully treating zinc-lead sulphides, and the metallurgy of zinc would be incomplete without a brief statement of at least some of them.

10. Mechanical Concentration. — The separation of zinc and lead sulphides by concentration has been practiced successfully in the Kansas-Missouri zinc district, where the two sulphides are in coarse crystals and can be broken apart. In the Leadville district, the success attending separation by concentration has not been so marked because of the fineness of the different minerals after crushing. The average specific gravities of such minerals as are commonly mixed with blende are galena, 7.4; pyrite, 4.85; chalcopyrite, 4.04; while the specific gravity of blende is 4. The marked specific gravity between zinc sulphide and galena is not sufficient to separate the minerals by water when they are fine grained, although a fairly good product has been obtained. With ore which carried 40 per cent. galena, 15 per cent. blende, 30 per cent. pyrite, the tailings after concentration of galena and iron contained 35 per cent. blende, 4 per cent. galena, and the balance pyrite and rock. Assays made from many thousand tons of zinc tailings, obtained from many different concentrators, show the best work done has been to reduce the lead to 2 per cent. in the tailings, while it has often run as high as 12 per cent. A saving of from 50 to 70 per cent. of the blende with considerable gold and silver has been obtained; however, it may be stated with fair accuracy *that when galena and blende are in fine-grained crystals, mechanical separation by water on a commercial scale is out of the question.*

BARTLETT PROCESS

11. The **Bartlett process** of modified smelting was described in *Lead Smelting and Refining* and consists in converting the lead and zinc in the ores to zinc sulphate, zinc oxide, and lead oxide, in which form they pass from the furnace and are condensed. The objection to this method is that the treatment of ores rich in zinc and poor in lead cannot be accomplished under three fire operations. The pigment, which is a mixture of lead and zinc oxide, is said to be dense and white, free from injurious impurities, fireproof, and in

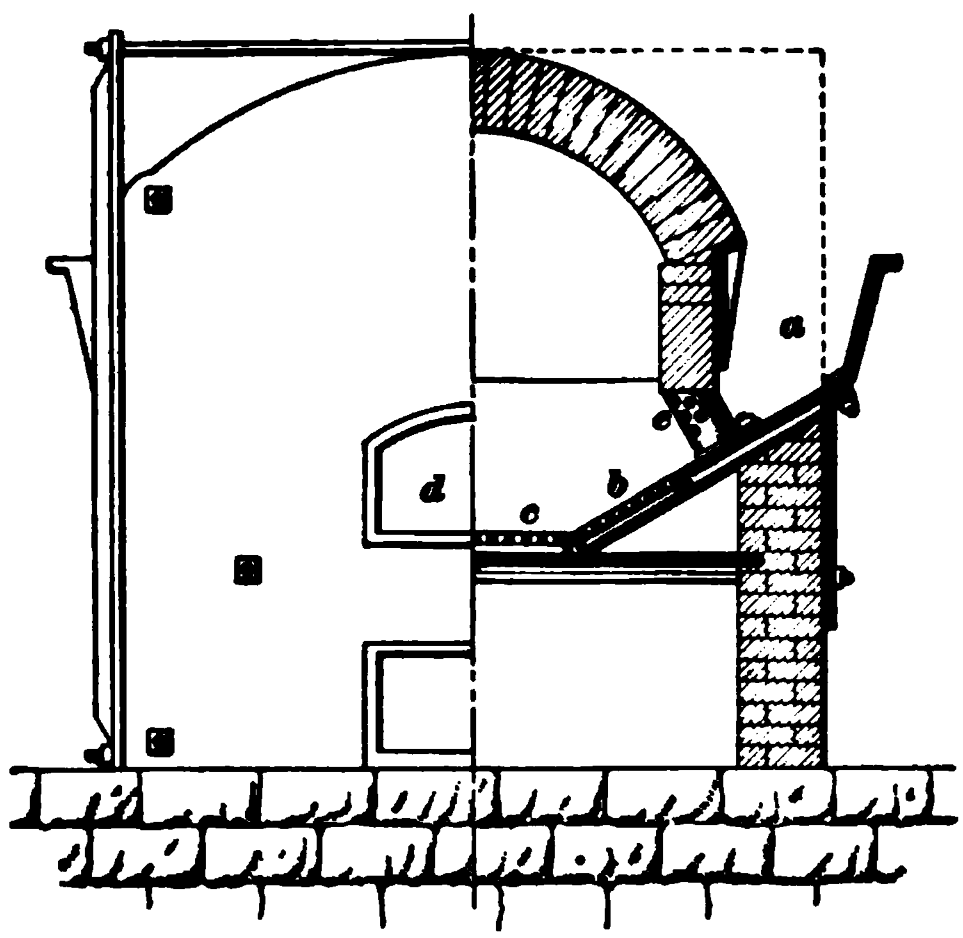


FIG. 1

no way resembling sublimed pigments. It is stated that the fuel required for the blowing-up process alone amounts to 15 per cent. by weight of the zinc in the charge. A front half section of Bartlett's blowing-up furnace is shown in Fig. 1. This furnace uses ore containing more than 20 per cent. zinc crushed to the size of pea coal and mixed with 15 per cent. slack coal. The mixture is charged into a pocket *a*, and as fast as the ore is sintered on the grates *b* and *c*, it is drawn off through a door *d*, fresh ore being dropped down from the pocket *a* to take its place. The air blast supplied

to carry on the operation enters the furnace through the grates *b* and *c* and also through the tuyeres *e*.

A perspective of one of the blowing-up furnaces at Cañon City, Colorado, is shown in Fig. 2. The sulphur from the ore can be entirely driven off if desired, but the main object

FIG 2

is to drive off the zinc and lead and sinter the ore sufficiently for the subsequent blast-furnace treatment. It requires from 20 to 40 minutes to drive off the lead and the greater part of the zinc and sulphur.

12. Volatility of Metals.—When mixed lead- and zinc-sulphide ores are exposed to an air blast in the presence of carbon, the lead is first driven off in the form of sulphate, sulphite, and sulphide. Experiments to determine the volatility of metals gave, when the ores were in a sulphide form, exposed to the action of incandescent carbon and air blast, the following order: mercury, cadmium, antimony,

lead, zinc. Bartlett states that lead can be wholly volatilized by expert manipulation and separated from zinc, but not as a commercial enterprise, on account of the difficulty of controlling the operation.

Fig. 3

13. Zinc Slag From the Bartlett Process.—The cinder formed in the blowing-up process contains zinc, silver, gold, and copper, with sufficient sulphur to form a small matte. The blast furnace in which the slag is smelted is shown in Fig. 3. It is low and the charge is fed on both sides from pockets, one of which, *a*, is shown beside the man in the cut.

14. Silica in Slag.—The rapidity of smelting in the Bartlett furnace is governed by the silica, that is, in case zinc is high in the slag, the fuel is increased and the silica raised, thereby causing slower smelting and less zinc in the slag. Zinc left in the cinder is always in the form of sulphide. Silicate of zinc is not formed, but oxide of zinc may be absorbed to a large extent, especially in the basic-iron slags. The following slag composition is given by Bartlett, where the aim is to reduce the zinc in the slags to as low as 6 per cent. metallic zinc or 8 per cent. oxide.

TABLE II

ZINCY SLAG ANALYSES

	Iron Slag	Iron and Manganese Slags	Iron and Lime Slags
SiO_2......	32.4 per cent.	36.2 per cent.	38.0 per cent.
FeO......	50.5 per cent.	34.7 per cent.	30.1 per cent.
ZnO......	15.2 per cent.	13.0 per cent.	11.4 per cent.
CaO......	....	4.0 per cent.	15.4 per cent.
MnO......	....	7.8 per cent.	3.1 per cent.
Ag ounces..	2.5 per cent.	1.5 per cent.	$\frac{1}{4}$ per cent.

15. Furnace Accretions.—With a low percentage of silica and a high percentage of iron, zinc absorption is high. High silica, low iron, and high lime give the lowest absorption of zinc. No evidence has been found of the formation of zinc silicate in the slags; the zinc seemingly fails to combine with any other element than oxygen. Both the silicate and sulphide of zinc are infusible in the blast furnace and tend to form accretions, which no amount of fluxing will dislodge. They are gotten rid of by running down low, then using large amounts of fuel and a heavy blast. This will decompose both zinc sulphide and silicate, forming oxides, which will pass off as fume. Oxidized zinc ores are easily

slagged off, if the ore is free from sulphur, but not otherwise, since, next to copper, sulphur has greater affinity for zinc than any other metal.

THE SADTLER PROCESS

16. Quite recently the treatment of Western complex zinc-lead ores has been satisfactorily accomplished by the **Sadtler process.** The ore is smelted in specially lined retorts in an ordinary Belgian furnace, and the results seem to justify the claims of the inventors. The retorts after being thoroughly dried in the usual manner are lined to a thickness of $\frac{1}{16}$ inch with a highly basic material, such as ilmenite or chrome iron, the lining being fastened to the retort material by sodium silicate. Ores carrying high percentage of iron or lead seem to have no injurious effect on the lining, though it is necessary that the silica be reduced, by previous concentration, to a minimum. At the Midland Smelting Company, Bruce, Kansas, where this process has been in use for some time, ores carrying as high as 30 per cent. iron and 10 to 15 per cent. lead have been successfully treated, without unusual injury to the retorts, the zinc remaining in the residue being reduced to about 8 per cent. The lead, iron, and precious-metal values are found in this residue, which constitutes a desirable material for silver-lead smelters. In theory, the iron and lead, being basic, have no effect on the refractory retort lining. In addition, the content of iron constitutes a valuable reducing agent by being first reduced to metallic iron, which, in turn, liberates the zinc by combining with the sulphur of any unroasted zinc sulphide. For this reason, it is claimed that the roasting has only to be carried to a minimum of 3 per cent. sulphur in the roasted ore.

MAGNETIC SEPARATION

17. Within the past year, the process of **magnetic separation** has been applied to complex zinc-iron ores with apparently great success, and as a result, large quantities

of the hitherto valueless ores of this character occurring in certain portions of Utah, Colorado, Wisconsin, and Missouri have been sufficiently separated as to make the products valuable alike to the silver-lead and zinc smelter.

By the use of the Wilfley concentrating table, no difficulty is experienced in reducing the lead content in these ores to 2 per cent.; hence the question to be considered is the separation of the two remaining constituents—zinc and iron.

In the Cleveland-Knowles process, the ore is first crushed to a size sufficient to free the two minerals, after which it is passed through a mechanical roasting furnace, where it is given a slight roast, at a low temperature, the object of which is to desulphurize the iron without appreciably affecting the blende. One hour is usually sufficient time to accomplish this. The ore after being cooled passes directly to specially constructed magnetic separators of high intensity, where the iron is extracted, the total extraction being from 94 to 97 per cent. of the whole amount originally present. The copper, precious-metal values, and most of the lead remain with the iron concentrate, thereby constituting a valuable material for the silver-lead smelter. Provided the original material has been well cleaned from foreign matter, the resulting zinc product contains an average of 60 per cent. zinc, not to exceed 1.5 per cent. iron. Plants for the treatment of complex ores by this process are now in active operation in Park City, Utah; Rico, Colorado; Cuba City, Wisconsin· and Joplin, Missouri, with the most satisfactory results.

MARKET FOR ZINC ORES

18. Those localities that are within reasonable distances of large smelters will possess a market for their zinc ores, provided they contain a fair percentage of lead, copper, gold, and silver. The treatment charge for zinc ores is based on the treatment of other ores plus an extra charge when zinc exceeds the limit of 12 per cent. The regular charge is 50 cents per unit above 12 per cent., a unit being 1 per

cent. of zinc in the ore. The Kansas and Missouri smelters running on almost pure blende will not purchase zinc ores if they contain more than 1 per cent. iron and 2 per cent. lead, neither will they pay for any gold, silver, or copper in the ore. The ores are purchased on a basis of 60 per cent. zinc and 1 per cent. iron, the basis being established each week by the buyers for the respective smelters, and is approximately 7 times the St. Louis quotation of spelter. Each 1 per cent. of zinc less than 60 per cent. and each 1 per cent. of iron in excess of 1 per cent. is penalized at the rate of $1 per unit, to be deducted from the basis. Lead in excess of 2 per cent. is penalized 60 cents per unit. The silver-lead smelter's opposition to ores containing much zinc is based on the loss of silver and gold that will occur owing to the volatilization of zinc.

REMOVAL OF ZINC BY CHEMICAL METHODS

19. Order of Procedure.—If sphalerite be roasted with an excess of air, the zinc will be converted partly into sulphate and partly into oxide. The former may be removed partly by leaching with water and partly by leaching with dilute acid. Blende is composed of 33 per cent. sulphur and 67 per cent. zinc, but when roasted only 23 per cent. is converted into zinc sulphate, while nearly all the lead present in zinc-lead ores is converted into oxides. There is evidence that zinc and iron combine in the roaster to form a double salt; thus, $ZnO + Fe_2O_3 = ZnFe_2O_4$, which approaches franklinite in composition if manganese is present. It appears an easy matter on first thought to roast zinc blende and leach out zinc sulphate, but on account of the high electropositive character of the metal, it is impracticable to precipitate zinc from aqueous solutions of its salts in a direct way. Metals that would precipitate zinc cost more for that purpose than the zinc is worth after precipitation. If lime, soda, or magnesia are used to throw down zinc from an aqueous solution, an enormous bulky precipitate, very difficult to wash and handle, is produced. The residue, which would

probably contain iron oxide, lead sulphate, gold, and silver, is left in a finely divided condition undesirable by most smelters.

20. Leaching Methods.—The usual method of procedure to leach and recover zinc from ores is as follows:

1. Roast at a low heat to form sulphate and oxide.

2. Leach with water to dissolve the sulphate formed by operation 1.

3. Heat with sulphuric acid in lead-lined pans.

4. Leach with water; add to the liquor obtained from 2 and precipitate any contained copper by means of scrap iron.

5. Evaporate to a paste and add to this one-fifth of its weight of finely powdered blende. This mixture, when calcined in a muffle, allows the sulphur to pass off as sulphur dioxide SO_2 and leaves the zinc as an oxide that may be smelted in the regular way.

6. The leached ore is calcined and the product forms an iron-lead-silver concentrate, suitable for lead-silver smelting. This process was introduced by Grimm in 1846, but was afterwards modified by Parnell, and is now known as the **Parnell process.**

21. The West Leaching Process.—The method of treating ores of zinc and lead sulphides known as the West process was quite successful in North Carolina, where it is said to have recovered 80 per cent. of the lead and 70 per cent. of the zinc from several hundred tons of ore, together with all the precious metals. The process consists of the following operations:

1. The ore is roasted, cooled, moistened with water, and placed upon a layer of pebbles in a false-bottom tank.

2. The sulphur dioxide SO_2 from the roasting furnace was forced up through the ore together with a jet of steam. This converted the oxide to sulphite, which in turn is converted into sulphate.

3. The ore is next removed to a separate vat and leached with water. The liquor thus obtained is drained from the ore and treated with a stream of gaseous ammonia to precipitate ammonium sulphate and zinc hydroxide; thus, $ZnSO_4 + 2NH_3 + 2H_2O = Zn(OH)_2 + (NH_4)_2SO_4$. The ammonium sulphate was next heated in a still with lime, thereby regenerating ammonia for future use.

4. The leached-out ore contained lead, iron, and precious metals, which were dried on an iron floor, under which passed the heated gases from the roasting furnace. When thoroughly dried, the residues might be considered a free-smelting concentrate.

RECOVERY OF LEAD FROM ZINC-LEAD-SULPHIDE ORES

22. Leaching Processes.—Various attempts have been made to leach the lead from zinc-lead-sulphide ores and then afterwards treat the residues for zinc and other metals that they may contain. One method was to treat raw crushed ore with hydrochloric acid, which attacks galena in preference to blende. Lead chloride thus formed is leached out with hot water and that metal precipitated by carbonate of lime, thus forming carbonate of lead. The tailings left from this process are smelted in the regular way for zinc. The percentage of recovery and the cost of this method of treatment are not stated, and as it has not come into general use, it is probably not practicable. Another plan for the treatment of lead-zinc ores in order to obtain the lead first, was to treat raw ore with hot hydrochloric acid and recover the zinc in the chloride solution after the lead had been thrown down. Such zinc-chloride solutions could also have their zinc precipitated by hydrogen sulphide, but the zinc sulphide formed is a difficult material to deal with. The zinc-chloride solution could better be broken up by electrolysis than by hydrogen sulphide, and in some instances this has been attempted with more or less success. All such processes, however, are covered by patents, and the prices charged by the patentee are sometimes such that they

prohibit their use. There have been so many of these lixiviation schemes patented and placed before the public that have proved failures on a commercial scale, although they were satisfactory in the laboratory, that many are afraid to attempt their use. Again, many schemes of this nature are advanced by men who know that they are not practical, and who use them as a bait for the purpose of trapping the unwary by their plausible appearance.

23. Leaching Lead From Roasted Ores.—Several attempts have been made to first recover lead from roasted ores by the use of hydrochloric acid. The lead obtained in such a solution is precipitated in one instance, at least, by metallic zinc. The zinc remaining in the solution is thrown down by lime. There are no records that show that this process has been practically adopted.

24. Alkaline Process.—Zinc oxide being soluble in alkaline solutions, attempts have been made to treat zinc-lead sulphides for the metals by such solutions. One process was proposed as follows :

1. Roasting the ore.

2. Leaching out the zinc sulphate formed with water.

3. Removing the residual zinc oxide with an alkali. The only cheap alkali for this operation is lime CaO, but as this substance forms a soluble compound with lead oxide, and in the presence of water forms calcium hydroxide, which is itself a precipitant of zinc according to equation $ZnO + Ca(OH)_2 + H_2O = Zn(OH)_2 + Ca(OH)_2$, it fails to effect the desired separation.

25. Ammonium Sulphate Process.—For this purpose the roasted ore is treated with ammonium sulphate and heated to 752° F., thus converting the zinc into sulphate. Ammonia is liberated, and the sulphates, if present, are leached out. Copper and iron sulphates, if present, are precipitated before the zinc by metallic zinc. The remaining zinc-sulphate solution is passed through towers, where it

is precipitated as zinc hydroxide $Zn(OH)_2$ by ammonia, and ammonium sulphate is regenerated for the next heating.

26. Chlorination Process.—When zinc-sulphide ores are roasted with salt, there is formed a zinc sulphate which may be leached out and converted into zinc chloride by the addition of calcium chloride.

If partially roasted blende be mixed with salt and re-roasted, much of the zinc will be converted into soluble chloride and may be leached out. Silver and lead will also find their way into the solution in appreciable quantities. Advantage is taken of chloridizing roasting to form soluble compounds, which are afterwards to be deposited by electrolysis.

27. Leaching Considerations.—The Parnell process involves the manufacture of sulphuric acid. This requires the expenditure of considerable money to carry it on successfully and is quite unsuited for operation in most sections. The cost of treatment is stated to be $6 per ton. The West process requires at least two treatments of the roasted ore with sulphur dioxide and steam, and as the leaching is done in other than sulphating vats, the handling becomes expensive. There must also be a blowing engine and an ammonia factory, so that taken all in all, the treatment of any large quantities of ore by the West process must be expensive, irrespective of the cost of the plant.

28. Solution of the Zinc-Lead Problem.—According to one writer, the true solution of the problem of zinc-lead-ore treatment will require that :

1. The treatment shall occur at the mine.
2. Complicated apparatus and skilled labor is to be avoided.
3. Rapidity of operation on the largest scale must be had.
4. Acids and reagents must not come from a distance.
5. Zinc must be removed, leaving the lead and silver.
6. The cost of treatment must be well below the market value of the products.

ELECTROLYTIC METHODS OF ZINC PRODUCTION

29. Direct methods of extracting zinc from sulphide ores being at present out of the question, many electrolytic-reduction schemes have been advanced, but none have, so far as known, proved effective. The precipitation of zinc as a secondary process by electrolytic methods is possible, but it has never yet been accomplished at such a cost as to allow the process to compete successfully with existing distillation methods; therefore, the only practical methods in existence are dry methods, and it seems at least open to question whether the cost of the electrolytic production of zinc can ever be reduced to such a point as to make it commercially successful.

30. The electrolysis of zinc has already been dealt with and is mentioned here for reference only. In business, the profit involved is the ultimate test of its success, and this applies to metallurgical ventures as well as others. In view of this, attention has been directed to the methods of lixiviating zinc ores only to give an insight into their so far unpractical methods. Wet methods have not proved themselves capable of extracting as large a percentage of the metal as the dry processes.

TREATMENT OF FRANKLINITE

31. Franklinite.—At Franklin Furnace, New Jersey, there exists a very large body of complex ore composed of several individual minerals, which has received the mineralogical name of **franklinite.** The composition of this ore varies as it comes from the mine, sometimes running higher in one mineral than usual and then again lower, or all the components may increase and decrease, but probably the following assay will represent a fair average: Iron sesquioxide, 32.06 per cent.; manganese protoxide, 11.06 per cent.; zinc oxide, 29.35 per cent.; carbonate of lime, 12.67 per cent.; silica and insoluble matter, 14.57 per cent.

The mineralogical composition of the ore is calculated to be as follows: Franklinite, 51.92 per cent.; willemite, 31.58 per cent.; calcite, 12.67 per cent.; silica and insoluble matter, 14.57 per cent.; zincite, .52 per cent.

32. The Converse Process.—To extract zinc economically from franklinite, Mr. Converse followed the method described below. Before the ore was shipped from the mines it was crushed to pass an 8-mesh screen and was then concentrated on Hartz jigs and round tables. The concentrates, which contained the zinc minerals, were separated into two classes, one of which went to the spelter furnace and the other to the zinc-oxide department. This separation was accomplished by mixing the ore with 20 per cent. of anthracite coal and charging the mixture into a brick-lined furnace heated by gas. After the ore had become bright red it was discharged into a revolving cooler. The ore, after cooling, was next passed over a series of magnetic separators; the non-magnetic material thus obtained was used for the manufacture of spelter, while the magnetic material concentrated was sent to the oxide furnaces. The non-magnetic material contained 46.38 per cent. zinc, 3.76 per cent. iron, and 6.68 per cent. manganese. The magnetic material contained 29.66 per cent. oxide zinc, 37.20 per cent. iron, and 9.34 per cent. manganese

33. The magnetic material was mixed with anthracite coal, and 83 per cent. of the zinc contents was distilled off, the remaining 17 per cent. with all the iron and manganese being left on the grates. The residue was next removed and smelted in the blast furnace, the product being spiegeleisen. The gases leaving the furnaces being heavily charged with zinc fumes, were conducted through pipes and condensed. The oxide produced was of a yellowish hue and could only be utilized for the manufacture of metallic zinc. The Converse process gave good results, but the cost of roasting and the uncertainty of a uniformly magnetic product led to the introduction of the *Wetherill process*. Another objection, based on the percentage of franklinite in the

retort zinc, was that the iron and the manganese of that mineral attacked the material of the retorts, thus destroying them quickly.

34. The Wetherill Process.—For this process the ore is crushed to .5 inch in diameter, after which it is dried. From the drier it passes to crushers, which still further diminish the size of the particles of ore, after which it is run over a Wetherill magnetic concentrator, which produces concentrates containing manganese and iron and tailings having a mixture of willemite, zincite, and calcite. The tailings are jigged in the ordinary manner to remove the calcite, the product remaining yielding a concentrate that produces a first-class spelter. These concentrates, which are obtained in a more direct manner than by the Converse process, average 50 per cent. zinc, 2.5 per cent. iron 4.5 per cent. manganese, and but a trace of lead.

ZINC DISTILLATION

35. The terms retorts and distillation have been unavoidably used in speaking of zinc recovery, and so far in the science of the metallurgy of zinc its practical recovery is based on the volatility of zinc.

The theory of the production of zinc in the dry way is dependent principally on the facts that zinc oxide, carbonate, and silicate are reduced to metallic zinc by incandescent carbon, and that metallic zinc is capable of distillation. The recovery of zinc on this basis is a matter involving many technical difficulties, particularly those of making retorts suitable for the work and the chemical behavior of the zinc due to the impurities in the ores. Again, special degrees of heat for distillation and condensation are required in order to obtain a pure product, as well as freedom from such impurities as will mix with the metal, since zinc refining is in no way a desirable adjunct to zinc production, if it can be avoided.

36. Blast-Furnace Smelting.—The production of zinc by ordinary blast-furnace smelting has not so far proved satisfactory. It is possible to produce zinc oxide in the blast furnace, but the vapors of zinc are necessarily so largely diluted by furnace gases under most favorable circumstances, that only the fumes of metallic zinc can be recovered. In the Wetherill process, the zinc left in the iron and manganese ore is vaporized and passes from the furnace, leaving the iron and manganese alloy in the form of spiegeleisen. While it seems probable that the blast furnace may in the future prove useful in the concentration of low-grade zinc ores by driving off the zinc as fume or oxide, it seems most improbable that zinc in the metallic form will be so produced.

37. Reverberatory Smelting.—There is no reason to suppose that the direct recovery of zinc can be accomplished in the reverberatory furnace. The reducing action in such furnaces cannot be made sufficiently strong to produce anything but zinc oxide. The necessities involved among other things is a very high heat approaching whiteness, or 2,200° F., for the reduction and at the same time complete separation from air, watery vapor, and furnace gases is desirable. On a commercial scale the treatment of zinc has been confined to a reduction by carbon and distillation without contact with air.

38. Distillation.—In this process so many objectionable features present themselves that the best efforts of those engaged in this branch of metallurgy have been required to put it into anything approaching a perfect process. This means that the zinc ore and whatever reducing agent is employed must be enclosed in such a way as to reduce access of furnace gases on the one hand and atmospheric air on the other to a minimum; and this involves the use of high-grade refractory materials, especially chosen with reference to the requirements, which are made up into vessels of peculiar construction. The reduction must be performed by a reducing agent that will yield the least possible amount of

diluting gases, otherwise the vapor of zinc will condense in powder form, instead of the liquid condition desired; and, again, the condensation to a liquid will take place only through a very limited range of temperature, certainly between 415° and 550° C. and possibly even narrower than this. At the best, the recovery of the metal is very imperfect compared with other metallurgical processes. If the loss of zinc runs as low as 10 per cent. of the amount present, the results are considered very satisfactory, while losses may run up as high as 25 per cent.

39. Zinc Losses.—Imperfect recovery is, to a certain extent, unavoidable and is distributed over several items, which include the incomplete condensation of the zinc vapors, due to the fact that a certain dilution of the vapors with carbon-monoxide gas is unavoidable and also to some penetration of the walls of the vessels in which the distillation takes place. The breakage of vessels containing charges of zinc ore occurs frequently, because the material of which they are constructed is fragile. It is impossible to remove all the zinc vapor from a retort at the conclusion of the operation, because it is impracticable to replace it by any inert gas; and, finally, the residues and even the walls of the vessels retain considerable amounts of the metal. There is also a considerable loss in zinc due to its combining with the alumina of the retort to form zinc aluminate, analagous to the mineral gahnite. This is evidenced by analysis and by the intense blue color of retorts that have been in use for a long time. It is very unlikely that at the intense heat at which the retort is maintained any zinc could be mechanically absorbed. It is said that before a retort will arrive at its maximum yield it will retain in this manner approximately its own weight of zinc. While each one of these sources of loss may be reduced to a comparatively small figure taken alone, in the aggregate they represent sufficient to make the extraction very faulty.

40. Chemical Behavior in Retorts.—Prost found that the reduction of pure zinc oxide ZnO is unaffected by ferric

oxide Fe_2O_3, aluminum oxide Al_2O_3, and lead oxide PbO, when the temperature is 1,967° F. Mixed with other oxides in equal molecular proportions, zinc oxide is unaffected even when the temperature reaches 2,205° F. Since zinc sulphide ZnS is decomposed by iron, there should always be an excess of the latter above the theoretical amount necessary for combination. With a mixture of ZnS and 190 parts of iron by weight, the zinc was volatilized at 2,205° F., while at 1,967° F. considerable remained in the residue. An excess of 75 per cent. lime over the necessary quantity for combination decomposed zinc sulphide completely at 2,250° F. Calcium sulphate at 2,205° F. had no retarding influence on the reduction of zinc oxide even in the presence of lead and iron silicates. Magnesium sulphate at high temperature is decomposed by carbon into magnesia and sulphur dioxide, and this favors the production of zinc sulphide.

41. The conclusions drawn from the experiments of Prost are that combinations formed during the combustion of carbon can be reduced at the ordinary working temperature of the zinc furnace; and loss in lead-bearing residues may be reduced by judicious admixture of lime in the charge. While iron is a valuable reducing agent for zinc sulphide, a quantity in excess of 6 per cent. has been found to damage the retorts to such a degree as to more than offset its advantages. In cases where the ore carries this quantity of iron, it is necessary to remove it by magnetic separation before treating or to use some of the special processes mentioned.

PREPARATION OF ZINC ORES FOR REDUCTION

42. Zinc-ore reduction involves either calcination or roasting, which operation is usually preceded by some other, such as crushing and concentrating, if the ores are mixed with other minerals.

Zinc-carbonate ores must be calcined in order to remove as completely as possible the carbon dioxide, which would

otherwise serve to dilute the zinc vapors and interfere with their condensation. Further than this, it will be remembered that carbon dioxide acts to a certain extent as an oxidizing agent on the metallic zinc, so that a considerable portion of the zinc vapor that distilled over during the evolution of carbon dioxide from the ore would be recovered in the form of zinc oxide instead of metallic zinc, as desired. *Zinc-silicate ores* are frequently hydrated, and, besides, contain more or less water carried mechanically. This must also be removed by calcining, since it would act similarly to the carbon dioxide if charged into the vessels with the ore.

43. Calcining.—For purposes of calcining, shaft furnaces with external fireplaces have proved most satisfactory. During this operation it is desirable to avoid mixing the ore with the fuel, since the ash would not only dilute the ore, but would be likely to introduce elements that would lead to trouble at a later period. The action of the reverberatory furnace for calcining is too slow and requires too much labor, for which reason shaft furnaces were adopted. Latterly, all types of kilns for roasting silicate ores have been abandoned in the best American practice, these ores being mixed with a larger proportion of roasted blende and coal and treated in the retorts. From this it would appear that before the temperature at which zinc is reduced is reached, the combined water of the silicate is driven off. In calcining, it must be remembered that the carbon dioxide is to be removed not merely from the zinc carbonate, but from any acid carbonates that may be present. It is the carbon dioxide itself that is objectionable, independent of the material with which it may be combined.

44. Roasting.—In the case of sulphide ores, roasting is an absolute necessity, as far as the present development of zinc metallurgy has gone. Direct reduction of zinc from its sulphide ores is yet to be accomplished on a commercial scale. On the closeness of the elimination of the sulphur by the process of roasting depends much of the success in

the treatment of sulphide ores, because if sulphur is left as zinc sulphate, and this is brought into the highly reducing condition necessary for the reduction of zinc oxide to its metallic form, the zinc sulphite is changed back nearly completely to the zinc sulphide and no further action ensues. *The successful roasting of zinc ores involves a much higher temperature than that necessary for the ores of lead.* The first products of the oxidation of zinc sulphide are zinc oxide and zinc sulphate, and the removal of the last traces of sulphur by decomposition of the sulphate into zinc oxide and sulphuric anhydride can be brought about only at a very high temperature. Fortunately, however, unless impurities forming fusible compounds are present to a considerable extent, there is slight danger of fusing or sintering ore, thus making its working in the roasting furnace a matter of very serious difficulty.

45. Roasting Furnaces.—The furnaces employed are of various types, both hand reverberatories and mechanical reverberatories being used. In localities where the production of large amounts of sulphurous gases would involve legal difficulties or where a ready market for sulphuric acid is obtainable, much zinc-blende roasting is done in muffle furnaces, in order to obtain the sulphurous gases in as concentrated a form as possible, that is, without dilution by the furnace gases, and then to utilize them in the manufacture of sulphuric acid. For this purpose, furnaces with several tiers of straight muffles, employing mechanical means for stirring and carrying forward the ore, and others of circular form, resembling somewhat the Herrschoff pyrite burner, are employed. Whatever the style of furnace or method of treatment, the principal aim must be to remove the sulphur as completely as possible, and this becomes one of the essential points of successful working. After roasting has been completed, the ore is thoroughly pulverized and mixed with a reducing agent; it is then ready to be charged into the vessels that are used for the reduction of zinc, as well as those used for its distillation.

46. Retort Fabrication.—Before taking up the reduction of the roasted ore, the vessels in which the distillation occurs are to be considered. On these vessels the success of zinc distillation depends as much as anything else, since losses will occur in case the retorts break, and it is along these lines that economy in zinc recovery has taken place to a large extent. There are two general types of vessels in use; one is round and cylindrical and is called a *retort;* the other is half round on top and is called a *muffle.* As each vessel is used for the same purpose, both will be called retorts in speaking of them, unless it becomes necessary to specially designate them otherwise. On account of the temperature to which the retorts are subjected, viz., white heat (2,832°F.), fireclay is the only material that has been successfully used in their construction. New clay is not used alone, but is mixed with *chamotte*, a material obtained from slagging and then crushing sandy clay. In America, the words "cement" or "grog" are used to designate this material, which is almost exclusively made from broken firebrick and raw clay molded into adobes and hard-burned.

47. Conditions Governing the Construction of Retorts.—Retorts must be made of such refractory material that they will resist intense heat and will not be corroded by slag-forming impurities in the ore. They must be so compact that zinc vapor will not penetrate them. They must be strong enough to retain their shape when charged with ore and supported at the ends only. The length of cylindrical retorts is about 4 feet and the inside diameter about 8 inches on an average, the thickness of the walls varying from $\frac{3}{4}$ to $1\frac{1}{2}$ inches. The length of muffles is from 4 to 7 feet, and they are from 7 to 8 inches in width and from 18 to 24 inches in height. While the conditions governing the construction of retorts require strength, they also require the walls of the vessels to be so thin that the heat of the furnace may penetrate them and act on their contents as much as possible.

48. Clay Retorts.—The suitability of fireclay for retort construction can only be determined by actual experiment.

The clay used in Missouri, Kansas, and Illinois for retorts is termed Cheltenham fireclay, and is obtained from a limited zone in St. Louis County, Missouri. It has the following composition: Pyrite, 2 to 3 per cent.; calcium carbonate, .4 to 1.25 per cent.; manganese, .05 to .9 per cent.; potash, .3 to 1.1 per cent.; sulphur, .1 to 1 per cent.; sulphuric anhydride, .1 to .8 per cent.; titanic acid, 1 to 1.8 per cent.; silica, 51 to 68 per cent.; aluminum, 19 to 31 per cent.; combined water, 8 to 12 per cent. The clay is coarse-grained and sandy, with the usual high density of coal-measure fireclay. To make a stiff plastic mass of the fireclay requires from 14 to 20 per cent. of water. When this mass dries in air, it shrinks from 6 to 9 per cent. and when burned it has an additional shrinkage of from 4 to 8 per cent. It can be heated up to 2,700° F. before failing. The average tensile strength of this burned clay is about 150 pounds per square inch, although at times it varies from 100 to 250 pounds per square inch by actual experiment.

One of the demands made upon clay is that it shall burn dense and finish free from rents. Such material is obtained by a mixture of chamotte with just enough raw clay to bind the chamotte grains. The most refractory material is chosen for this purpose and it is just such a fireclay that has the greatest shrinkage. This is overcome by a judicious mixture of old and new material. It is important that the clay contains no outside matter, such as pieces of rock, inasmuch as the unequal expansion would split the retort when in use. Old retort material is of limited refractoriness. Retorts containing a high percentage of it bend and break, and those in which it is at least in part replaced by good chamotte are stronger. In some instances shale is substituted for old retort material with marked success. Coarse chamotte is mixed with fine kaolin, which has sufficient fat to answer as a binder for the lean material. The coarse grains of chamotte help the retort to withstand sudden changes in temperature and make them less liable to corrosion. In one Belgian works, 40 parts by measure of dark, fat, raw clay is mixed with 50 parts of light-colored sandy clay burned to chamotte

and 10 parts of coke. Another uses 30 parts fat, raw clay; 10 parts raw, sandy clay; 50 parts old retorts ground up; and 10 parts of coke. This last mixture is said not to be as durable. In American practice, retort material consists wholly of raw and burned clay, or "cement," in the average proportion of 7 parts raw clay, 9 parts cement, and $3\frac{1}{2}$ parts water.

49. A predominance of alumina rather than silica seems to be desirable for zinc retorts, and the practice which prevailed at one time of adding silica to the fireclay mixtures was found disadvantageous and has been discontinued. The true value of fireclay, however, can never be predicted with any certainty by a purely chemical examination; so much depends on the state of chemical combination in which the ingredients are present. It seems to be well determined, however, that silica and alumina, in the proportion to form silicate of alumina, is undesirable, since retorts made from this material have a tendency to bend when in use. Fireclay as mined is not sufficiently strong and shrinks too much on heating to make it desirable to use exclusively in constructing the vessels. It is strengthened and stiffened by the addition of other materials or of fireclay that has already been burned and has thereby lost its water of hydration and with it its plasticity and tendency to shrink. The present practice in the United States is to make up a mixture of approximately equal parts of burned clay and raw clay, and the introduction of other materials, such as brown coke, silica in the form of sand, etc., has been largely discontinued. If anything, the burned clay in the mixture is in somewhat larger amount than the raw clay.

50. In this country the vessels are all of the Belgian or retort style and great improvements in their manufacture have been effected by the use of machinery, which forms the vessels under high pressure and renders them less permeable, either to furnace gases from without or to zinc vapor from within. Formerly, they were built up entirely by hand; now hydraulic presses are used, giving much more

compact walls. The vessels made by the new method also last somewhat longer in the furnace than did the old hand-made type. In both cases the preparation of the material is about the same; for example, raw clay is thoroughly ground and disintegrated, mills of the edge-runner type being well adapted for the purpose. The burned clay, usually the broken retorts from previous operations, is crushed—not ground—and both the burned and raw materials thoroughly incorporated. The sized grains to which old retorts are crushed is governed by two considerations: the grains must be small enough to avoid excessive porousness in the finished vessels and large enough to impart the desired strength. The usual size is such as will pass a 6- or 7-mesh screen of No. 16 wire. To the proper proportions of raw and burned clay sufficient water is added to give the mass plasticity; this is then thoroughly worked in a pug mill of the ordinary type until a uniform mixture has been secured. Greater plasticity is obtained by allowing the mixture to stand in a bed for several weeks, with occasional sprinklings of water to avoid drying out. The longer the material can remain in this condition, without undue drying, the better will be the retorts made from it.

In working up retort material, the procedure is as follows: 7 parts of ground clay and 9 parts of ground "cement" by volume, are thoroughly mixed with 3½ parts of water, also by volume, and shoveled into a stock pile. This constitutes a "batch," and will, when the measure of volume is an ordinary water bucket, make three retorts. When the stock pile is of sufficient size, it should be allowed to remain over night and passed through the pug mill the first thing the next morning. It can then be covered with damp cloths, and provided it does not dry out, will improve with age. When retorts are to be made, this material is put through the pug mill a second time, as needed.

51. Hand Construction of Retorts.—If hand construction is to be practiced, the clay is beaten out into slabs by means of mallets; these slabs are then brought to the desired

conformation by placing them in iron molds of the shape of the finished vessel. The retorts are thus built up in sections.

One section of the mold receives a slab of clay, which is tamped with an iron rammer until the clay has been made to fill the mold properly. The surface of the clay that is to form the joint with the next slab is roughened, so that firm adhesion may be secured; then, the next section of mold is put in place and the corresponding slab of clay beaten in. This is continued until the whole retort has been built up. The vessel now being shaped, it is allowed to remain in the mold for a day or two, to let it become firm enough to retain its shape, the vessels are then removed and a thorough air drying in a heated and well-ventilated room follows.

In this last operation the temperature is gradually increased through a period of about two months. Generally speaking, the longer the retort remains in the dry room, the better it will be. All drafts producing unequal drying must be carefully avoided.

52. Machine Construction of Retorts.—For the modern method of retort construction the clay is forced into shape by hydraulic pressure, various types of machine and die being used. Two general principles control their construction, however—either the clay is forced through as a continuous stream by hydraulic pressure and the closed end to the cylinder is attached afterwards in a separate press, or the whole vessel is formed from one piece of clay by forcing a plunger in to form the interior. In the latter case the material displaced rises and forms the side walls. The hydraulic method not only forms denser walls to the retorts, but is so much quicker that it has practically displaced hand-made retorts, at least in this country. The subsequent treatment is the same as for hand-made retorts. It may be mentioned that no kiln drying successfully replaces the slow uniform air drying already mentioned. After air drying, the vessel must be heated slowly and thoroughly to a red heat in kilns or furnaces erected for the purpose, and the

retorts and muffles are introduced into the distillation furnace at a red heat.

53. Life of Retorts.—Sometimes certain foreign materials in zinc ore have a damaging effect on the retorts. This is particularly the case when fusible silicates are formed, as they will cut through the fireclay and destroy the vessel. The composition of fireclay is silicate of aluminum and this in itself is extremely refractory. Silica alone, therefore, will not be liable to cause any damage if present in the gangue. If, however, bases are present with the silica, which have the possibilities of forming fusible complex silicates, the danger is increased. Iron, especially, is bad, or iron and the alkaline earths together. In this fact will be found an answer to the question which may have presented itself in connection with the possibilities of recovering metallic zinc from its sulphide by the formation of metallic iron. Such a reaction would result in the production of ferrous sulphide FeS, which would then be free to attack the fireclay and penetrate it. The effect of sulphides of iron on fireclay may be seen in the black spots that are to be noted, especially in the poorer grades of fireclay. These are due to particles of pyrite, which are often present in the fireclay, and a very small amount makes a very considerable showing in the black spots produced. If in greater amount, the fireclay is rendered useless, because the double silicate of iron and alumina thus produced is so fusible as to destroy the practical value of the fireclay. Lead was formerly considered very dangerous to the life of the vessels, but in the form of oxide it is so quickly reduced that unless present in excessive amounts the formation of lead silicate is very slight. If such a silicate forms to any extent, however, it is so extremely fusible that great injury results. Unless the lead is in the metallic form, no further action between it and the fireclay takes place. On account of the danger of forming fusible silicates, a desirable plan to follow is to classify the ores according to the properties of their gangue, that is, to include in one class ores containing silica in excess

and in another those with a base gangue. In this way the life of vessels may be considerably increased. Lime and magnesia alone do not give any particular trouble.

54. Shape of Retorts.—The cylindrical retorts shown in Fig. 4 are closed at one end *a* and left open at the other *b*,

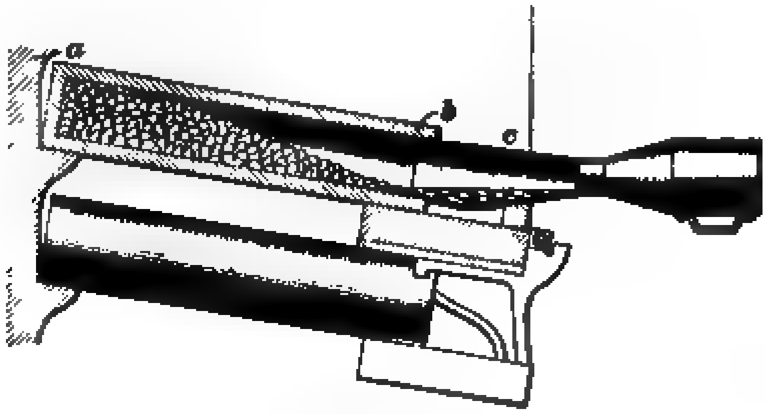
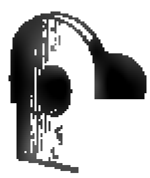


FIG. 4

in order that they may be charged with coal and ore. The open end is closed after the charge has been inserted by the introduction of a condenser *c*, called an *adapter*. The muffles shown in Fig. 5 (*a*), (*b*), and (*c*) are closed at one



(*b*)

FIG. 5

end when they are constructed, and the other end, Fig. 5 (*c*), is closed by a tile *c* during their use. The adapter is fitted to the tile, shown in Fig 5 (*b*), as in the case of retorts.

The different shapes given these retorts depended on the character of the fuel prevailing in the localities where the vessels were first used. The round retort is known as the *Belgian*, and as the coal in that country was of the long-flaming variety, it was found desirable to so arrange the furnace that the heat of the flame could be utilized to the best advantage. Large furnaces were constructed which were filled with a number of tiers of retorts supported entirely from the ends. The number of retorts to a furnace varied, according to the whim of the designer, from 100 to 200 in a single furnace. In this country the standard size is 112 retorts per furnace. On the other hand, in Silesia, the coal was of the short-flaming variety, and its heating power was confined to a much smaller surface; therefore, the furnaces were built low and so arranged that the vessels, muffle-shaped in this instance, were supported from beneath along the entire length, while the heat was deflected upon them from the roof above. Originally, only one pair of muffles was placed in the furnace, but since the introduction of gas-fired furnaces, tending to approximate to the properties of long-flaming coals, the number of tanks, or tiers, of muffles has been increased to two or sometimes even three, in the case of small sizes. The retention of the muffle-shaped vessel is merely a persistence of the original design necessitated by first conditions. In the manufacture of condensers, a poorer quality of clay is used than for retorts. The cement with which this clay is mixed consists of old retorts from which the silicious coating has been removed and broken condensers. The raw materials are crushed to the same size as are those for retort purposes. The mix is made in batches, as before, the proportion being 8 parts clay, 9 parts cement, and 4 parts water, by volume. Each batch will suffice for about 60 condensers.

After being well mixed, the mass is allowed to rest over night, then passed twice through the pug mill the next morning, and the mass covered with damp cloths until the next day, at which time it is in suitable condition to work. The condensers are made by molding the clay by hand into

cones, which are placed in sheet-iron molds of the dimensions of the outside of the condenser. An iron plunger having the dimensions of the inside of the condenser is then forced into the mold, producing the desired shape. The condensers are removed from the mold to the drying room, and when they have dried to a sufficient degree, the larger ends are contracted by compression, after which they are thoroughly dried. Finally, they are fired at a red heat for about three days. Before use they are given a coat of whitewash on the inside, to facilitate the removal of dross after their use at the furnace has been discontinued.

55. The Reduction of Zinc.—For the purpose of reduction, roasted, or in some cases calcined, zinc ore is placed in retorts with coal and heated to a white heat. The zinc in the retorts is present either as zinc oxide or zinc silicate; of the two, zinc oxide is much more readily reduced. When heated in association with carbon, the first reaction will be $ZnO + C = Zn + CO$. This carbon monoxide CO formed at once acts as a further reducing agent by the reaction $ZnO + CO = Zn + CO_2$. If no further amounts of carbon are present, this latter action will be limited by the equilibrium which would be established between the carbon monoxide and carbon dioxide; but since there is an excess of incandescent carbon present, the carbon dioxide is at once reduced to carbon monoxide by the familiar reaction $CO_2 + C = 2CO$. This, in turn, reduces further amounts of zinc oxide, to be itself reduced from its dioxide form to the monoxide by further amounts of carbon.

It will be seen that the secondary products of the reaction are carbon monoxide and metallic zinc, which at the temperature of the reaction is in the form of vapor. The production of such amounts of carbon monoxide creates a pressure in the vessel, and a mixture of carbon monoxide and zinc vapor issues from the mouth of the vessel into the condenser, which is attached to its throat and which extends outside of the furnace. Ordinarily, the proper temperature for the condensation of zinc in its liquid form is between

415° and 550° C., and while the zinc is deposited the carbon monoxide escapes from the adapter either directly into the outer air or through a sheet-iron nozzle, which serves the further purpose of collecting particles of zinc that may be present in the form of powder. If the temperature exceeds 1,022° F., the zinc vapors will not be condensed. The arrangement of vessel, adapter, and nozzle is shown in Fig. 6. The retort *a* is connected with the large end of the adapter *b*, while the other end of the adapter is covered with a sheet-iron nozzle *c*.

56. If the zinc is in the form of silicate, it is reduced only by contact with incandescent carbon, and, therefore, in such instances requires fine grinding and careful mixing with the carbon used. Should any zinc sulphate be present, it is reduced to zinc sulphide by the carbon, in which form it remains unchanged throughout the operation unless it be acted on by the metallic iron that may be reduced from iron oxides in the gangue. Other materials that may be present act on the zinc compounds themselves merely as dilutants and interfere in that way with the close extraction of the zinc. Since the carbonates are porous, they need not be exceedingly fine. The silicates should be reduced to a small size, about 25 mesh, since they require to be brought into contact with the carbon. If retorts are used, finer crushing is necessary than in the case of muffles. Roasted blende is harder to reduce than calcined carbonate, and therefore should be crushed somewhat finer. In the United States, the best results are attained by crushing blende ores to pass 6 to 8 mesh.

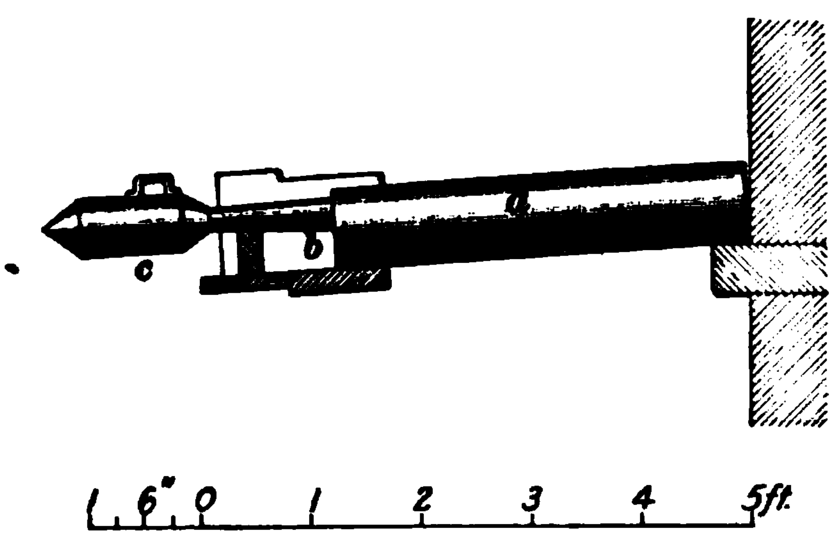


FIG. 6

57. The ore is next mixed with the carbon, which is added in the form of lean coal or coke. In the case of American practice, it is found desirable to have a certain proportion

of flaming coal present. To this end, coal low in volatile carbon and sulphur, such as crop coal, is mixed with the crushed coke in the proportion of $\frac{1}{3}$ to $\frac{2}{3}$, or in equal amount. In certain cases, where the crop coal is of a high quality, good results are attained without admixture of coke. In theory, the volatile matter of the coal will be driven off before the zinc is reduced, and thus effectively wash from the retort all traces of air. The coke is made from ordinary bituminous slack coal by burning about 56 hours in beehive ovens. Before use, the coal-and-coke mixture is crushed so that the coarser lumps will pass $\frac{1}{2}$ mesh. In the more modern smelting works, thorough and uniform admixture of coal and ore is obtained by the use of screw conveyers or other mechanical mixing devices.

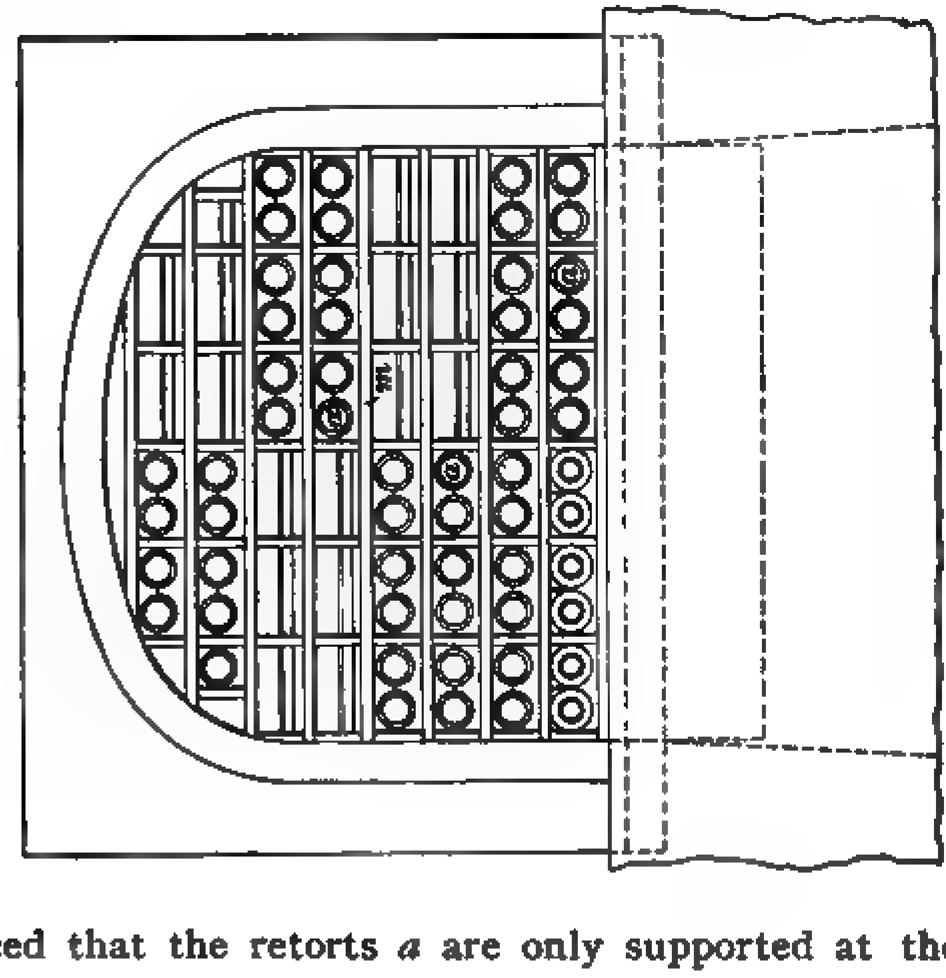
The mixture should be thorough, in order to bring the particles into intimate contact as far as possible, and sometimes, especially in the case of silicate ores, the crushing or grinding is completed after the addition of the reducing material. In any event, the finer the reducing material, the more efficient its action. The reason for using carbonaceous substances that will give off little or no gas is that rich bituminous coal will contain hydrocarbons. While these would serve efficiently as reducing agents in the first instance, they would give rise to the production of water, and, as has been shown, the effect of water on the reduced zinc would be injurious and cause oxidation. The amount of coal or coke added varies in weight from one-third to two-thirds that of the ore, depending on the percentage of zinc present and the relative ease or difficulty with which the reduction is effected. Naturally, the more difficultly reducible ore requires the larger proportion of reducing material.

BELGIAN METHOD OF ZINC EXTRACTION

58. Belgian Furnace.—The retorts used for the reduction and distillation of zinc by this method are supported at the ends and are limited in size, since if too long or too large in diameter, they would not be sufficiently strong when

heated to a white heat. In Fig. 7 (*a*) is shown the front view of a Belgian furnace with a flat grate. Fig. 7 (*b*) shows a vertical cross-section of the same furnace. It will

(b)



(a)

FIG. 7

be noticed that the retorts *a* are only supported at their ends by the projections *b* on the rear walls and the ledges *c* on the front walls of the furnace. The object of this construction is to permit heat to reach the retorts by

circulating around and between them unobstructed and to facilitate the removal of the retorts whenever necessary. It will be observed that the retorts are inclined towards the front wall, so as to facilitate the removal of the residue left after the ore has been deprived of its zinc contents. The adapters *d* are shown luted to the retort at one end and having sheet-iron nozzles *e* at the other. In order that the adapters may have firm supports to rest on, firebricks *i* are placed under them. These bricks rest upon the cast-iron plates *m*. The flames generated on the grate *n* pass upwards and out of the furnace to the stack *o* through the flue *p*. This is called the single furnace with one shaft, but furnaces are now generally built with double shafts, the two shafts being separated by a vertical firebrick wall.

59. Adapters.—Before charging the retort, the adapter is, of course, removed and only after the charge is inserted is it luted in place, as shown in Figs. 4 and 6. It is possible with adapters to maintain the temperature required for the condensation of zinc in its liquid form. If they were constructed of material that conducted heat more readily, they would become too cool and only the pulverulent form of zinc would be recovered. In order to save metallic particles, sheet-iron nozzles are attached to the adapters, so that the carbon monoxide produced during distillation does not burn directly after passing through the nozzle.

60. As shown in Fig. 7, the furnaces are so constructed that the retorts are arranged in rows one above the other, thus allowing the flame from the coal at the bottom of the compartment in which the retorts are placed to pass up and around their entire surfaces. The number of rows, which is usually from five to nine, is only limited by the fact that the temperature attainable at the top of the furnace decreases with its height until the top rows cease to be hot enough to carry out the reactions necessary. The number of retorts in a row varies with the size of the furnace and the length of the grate that can be efficiently fired. In the figure, they

are limited to twelve, although under certain circumstances they may exceed this number.

61. Since access is required to only one end of the retort, a saving in both heat and space is effected by building the furnaces double; that is, they are divided vertically through their length by a wall, upon either side of which are constructed ledges by means of specially shaped firebrick to serve as supports for the inner ends of the retorts. One form of brick thus used is shown in Fig. 9 (*b*), and another in Fig. 10 (*a*). The front of the furnace is a framework, shown in Fig. 9 (*b*), so arranged as to support tiles made of fireclay, described in Art. **58**, upon which the open or adapter end of the retorts rest, and also the adapters as well. There are two flues *b* in each compartment, which connect with the stacks *c*, as shown in Fig. 8. The retorts in the lower tiers are more apt to break than the others, and one or two rows are, therefore, frequently left empty and so arranged that the air supply for the grates is drawn through them and thus preheated. The upper row, which is the least strongly heated, is usually

FIG. 8

charged with the most easily reducible mixture of ore available.

62. Operating the Belgian Furnace.—If the furnace is a new one or contains only new retorts, it is run at a moderate heat for two or three days without introducing any charges into the retorts, since in this way those that are damaged or imperfect can be thrown out without loss, while the sound ones are put in much better condition for use. During this period no retorts are in place in the bottom row, but are introduced at a red heat after the furnace has reached its normal temperature. When ready for charging, the retorts are without adapters, and the mixture of ore and reducing material is introduced by means of long-handled shovels having the form of half cylinders and similar to those used in charging coal into gas retorts. Each retort is filled full, for any air space left is worse than wasted; the air contained at the beginning serves to change metallic zinc into zinc oxide, and at the conclusion of the operation, it is filled with zinc vapor, which cannot be expelled by any means yet devised in such a way as to be recovered. The two upper rows or cooler portions of the furnace are usually reserved for the "blue powder" or finely divided zinc, which collects in the condensers. This is mixed with the requisite quantity of coal and charged in the usual way.

63. An average-sized retort holds rather more than 100 pounds of the mixture of ore and reducing material. The more difficultly reducible the ore, the finer it should be crushed and the more reducing material should be added. The other factor governing the amount of reducing material is, of course, the amount of zinc oxide present in the ore. The retorts on becoming heated soon show the flickering blue flame of burning carbon monoxide at the mouth of the adapters. This is allowed to continue until zinc begins to come over in such quantity as to impart to the flame its characteristic greenish-white color. The sheet-iron nozzles are then attached to retain this zinc in metallic form as far as possible, though in any case it will be recovered in the

pulverulent form or in a finely divided state. In this country, these nozzles, or "prolongs," as they are called, are seldom, if ever, used, as the small quantity of zinc recovered by them is about offset by the cost of manipulation.

64. Effect of Carbon Monoxide on Distillation.—When the temperature required to bring about the desired interaction between carbon and zinc oxide or silicate is first reached in the retort, the amount of carbon dioxide, air, and water vapor present is such that the metallic zinc given off is oxidized again almost as soon as formed, and vapors of metallic zinc do not come over into the adapter until the atmosphere of the retort is almost entirely carbon monoxide. Even then that which first comes over is so diluted that it condenses as powder, and not until the furnace has been in operation for some time does the liquid zinc begin to accumulate in the adapter.

65. The time required for the treatment of a charge varies from 12 to 24 hours, depending on the position of the retort and the quality of the ore. On this account the men work in 24-hour shifts at many plants, in order to carry the charge through to completion without dividing the responsibility.

66. Tapping.—The molten zinc may be removed or **tapped,** as it is called, once or several times for each charge, depending on the richness of the ore and the capacity of the adapters. Tapping is done by men, who remove the nozzles and then with a hoe-shaped iron tool draw out the contents, dross, powder, and fluid zinc into a ladle held beneath. A movable staging is provided, on which the workmen stand when tapping the upper retorts. The ladle into which the products of distillation are drawn is of such a size as to hold just enough zinc to fill the molds in use. When the ladle is full, the dross powder and oxides are skimmed off to be returned to the upper banks of retorts with the next charge, while the clean zinc is cast into a flat-shaped slab weighing usually from 40 to 50 pounds.

In many works the ladle is of a capacity to hold about 250 pounds of molten zinc, and is suspended by chain falls from a carriage moving freely on an overhead track close to, and parallel with, the furnace front. With this appliance, the removal of the zinc can be accomplished with great dexterity and dispatch.

67. Clean-Up.—At the conclusion of the distillation the adapters are removed and cleaned, the old charge withdrawn from the retorts, and any retorts that are broken or seem likely to break during the next charge are replaced by new retorts, thus leaving the furnace in proper condition for the next shift. In some works a sheet-iron curtain, which can be raised or lowered, is provided, in order to protect men from the extreme heat when drawing the molten metal or when access to the furnace is not necessary.

68. Percentage of Recovery.—By distillation, from 85 to 90 per cent. of the zinc present in the retorts should be recovered, if the ore has been reasonably rich, say 40 to 50 per cent. zinc, and the retorts have been well and properly made and heated. With low-grade ores and imperfect treatment, the loss may run up to 20 per cent. In works where well-made hydraulic-pressed retorts are used, an average of $2\frac{1}{2}$ per cent. of the retorts and 8 per cent. of the condensers are replaced at the conclusion of each charge.

69. Fuel Required.—The quantity of coal required for each ton of zinc produced varies from 3 to 7 tons. With good work the average is in the neighborhood of 4 tons of coal per ton of zinc. For purposes of reduction, the amount of coal varies from $\frac{1}{3}$ to $\frac{2}{3}$ the weight of the ore. A low-grade ore requires more reducing agent in proportion to the zinc produced than does a high-grade ore, on account of the necessity of maintaining a highly reducing atmosphere in the retort, no matter what other conditions exist.

GAS-FIRED FURNACES

70. Gas for Fuel.—The Belgian retort system is almost wholly used in the United States, but instead of coal, gas has been introduced for fuel, thus producing a more efficient heat. If natural gas is not obtainable, producer gas may be substituted with very favorable results, although it does not contain more than one-half as many heat units for a given quantity as natural gas. Producer gas is formed by a partial combustion of coal brought about by an insufficient supply of air. This combustion may be effected in an entirely independent furnace known as a gas producer or on a grate placed beneath the chamber containing the retorts. In either case, air for complete combustion is supplied in the fireplace proper and the heat used is that derived from the burning carbon monoxide. The fuel may be anthracite or bituminous coal, since it is possible to use a very inferior grade of coal in the producers and yet obtain an efficient and readily controlled supply of gas.

71. Gas-Fired Furnaces.—Up-to-date zinc furnaces, that is, the newer furnaces, are all gas-fired. In the shape and general arrangement of these furnaces are to be found the principal improvements which have been made in zinc metallurgy in recent years, and each company is very jealous of its own types and modifications. Success has been attained by decreasing the height and increasing the length of the furnaces. In the Kansas gas fields, the standard size of a gas-smelting furnace is 600 retorts, or 1,200 retorts to a block of two furnaces. The introduction of long furnaces has been made possible by the substitution of gas for fuel, as this can be admitted in as many different places as is thought desirable.

72. Regenerators.—A further improvement has been proposed in the application of Siemens's regenerators to recover the heat otherwise lost with the waste furnace gases, which go to the stack at a high temperature unless some means of regeneration is employed. By the Siemens system

the hot gases pass through chambers filled with firebrick piled to form an open checkerwork. As soon as the contents of one of the regenerator chambers have been highly heated by the waste gases, these are shut off, and the air to be used in the combustion of the fuel gas is passed through the brickwork, thus heating it to a high temperature and raising nearly proportionately the temperature attainable by the chemical union of the gas and air. The passage of air over the heated firebrick of course cools them; but in the meantime the hot products of combustion have been passing through another similar chamber, one of the series just mentioned, and by the time the first is too cool to be effective the second is heated ready for use.

The heat thus recovered and returned to the distillation furnace in available form would otherwise be entirely wasted; connecting this with the fact that for every ton of zinc produced an average of 4 tons of coal are used as fuel alone, the possibilities of such an economy may be imagined. Up to the present time the regenerative furnaces have not come into general use, the great drawback being that when a retort breaks the zinc contained is burned to zinc oxide and carried over into the checkerwork, which thus becomes clogged. It is probable that means will be devised to overcome the present difficulties connected with regenerative firing, for the amount involved is too great to be neglected.

73. The Hegeler Gas-Fired Furnace.—Air for the combustion of gas is admitted at one end of this furnace. The air is all admitted at once and the gas at intervals towards the chimney end, so that in case the gas is high in hydrocarbons and from an insufficient supply of air would cause soot to deposit on the retorts and obstruct both heat and draft, it may be regulated. Ordinary furnaces admitted the gas at one end and air at intervals. This character of furnace was difficult to regulate. The construction of the gas-fired furnace at the Mathiesen and Hegeler zinc works is shown in Fig. 9 (*a*) and (*b*). The furnaces are double, with gas entering them from above. The gases

pass into the horizontal flues *a*, then into the vertical flues *b* on either side of the furnace, and finally escape through the

FIG. 9

apertures *c* into the upper part of the furnace. They here meet a blast of air, which enters the furnace through the

(b)

FIG. 20

(a)

tubes *d* and the slots *e*, these being connected with the blast main *f*. The products of combustion escape through the flues *g* below the retorts, and so into the flues *h* and *i* to the stack, which is not shown. The heat from the flues *h* and *i* assists in raising the temperature of the gas in the flue *a* before it enters the furnace.

74. The modern furnaces at these works are built somewhat different from those shown above. A fairly good representation of the most recent Hegeler furnace is shown in Fig. 10 (*a*) and (*b*). In the cross-section Fig. 10 (*a*), the brick air flue *a*, which joins the combustion chamber, is shown; also the retorts *b* as they are arranged in rows in the combustion chamber, with spaces *c*, shown better in Fig. 10 (*b*), between them. The supply of gas is furnished to the combustion chamber by a series of small pipes *d*, which are connected at one end with the gas main *e* and by means of holes *f* in the wall of the retort chamber. Similar pipes *g* enter the brick portion of the air flue *a* through holes *h*, so arranged that they may be luted air-tight with clay. Similar gas pipes in the front of the furnace are left on a loose joint so that they may be pulled out of their holes whenever it is desired to look into the furnace. Each gas pipe is provided with a valve to regulate the flow of gas and consequently the heat. In longitudinal section, *a* is the combustion chamber, *b* are the retorts, *c* the spaces between the retorts, *d* the small gas pipes entering *c* and the sides of the combustion chamber. Only the quantity of gas needed to heat the retorts in advance is admitted through these pipes, so that free oxygen is met by the gas entering the chamber at each section. The air, which may be either hot or cold, is forced through sheet-iron flues *i* with a fan and is distributed to the brick air flues by sheet-iron pipes *j*, which enter the walls as shown. The heat of the escaping gas assists in heating the lower retort. Furnaces of this description hold from 24 to 70 muffles, and when fired with groducer gas economize in coal, for with a good Mond gas producer, as much as 75,000 cubic feet of gas can be

produced from 1 ton of very inferior coal. The furnaces are also made double in some instances and are supplied with regenerative stoves, already described.

THE SILESIAN METHOD

75. The variations between the Belgian and the Silesian methods of zinc distillation consist in the shape of the retorts and the furnaces used for heating them, the principle being the same in both instances. The differences in small details between the two operations are made necessary by the changes in apparatus. Considerable variation in the construction and shape of the adapters exists, the essential purpose, however, the provision of a chamber which may be maintained at the temperature required for the condensation of liquid zinc and at the same time afford exclusion of air, is the same, and the variations are largely matters of whim or individual prejudice. The muffles are supported from beneath and usually throughout their length; this makes it possible to construct them much larger, and many of them will contain in the neighborhood of 200 pounds of ore, besides the coal necessary for reduction. This increase of size makes it not only practical but desirable to introduce the ore in a somewhat coarser condition, in order to avoid excessive density of the charge. The furnaces are built lower than the Belgian type and the heat is reflected on the tops and sides of the muffles. The true Silesian type has but one bank of muffles; but furnaces have been built with two and even three banks of muffles. The firing, which was done by using short-flame coal, is now better done by means of producer gas, just as in the Belgian furnaces, and the remarks in regard to the use of regenerators apply equally well to the case in hand.

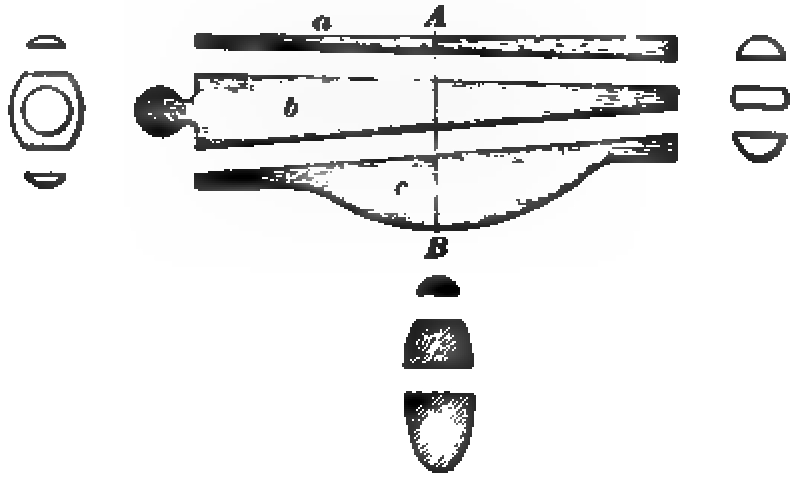
76. Muffles.—About 24 hours is required to complete the distillation of a charge. The difference in recovery seems to favor the Silesian muffles on low-grade ores rather than the Belgian retorts; the fuel consumption, however, is nearly the same, although the breakage of muffles is somewhat less. The latter fact is somewhat compensated by the

extra cost and difficulty in manufacturing muffles. In Fig. 5 (*a*) is shown a perspective of a muffle. Fig. 5 (*b*) shows a slab of clay provided with a short cylinder. This slab closes the upper part of the muffle and permits the end of the muffle and adapter to fit snugly into it.

77. Adapters of the shape shown in Fig. 11 allow the

Fig. 11

fluid zinc to collect in the hollow, and from this hollow to be raked out from time to time. With such adapters, a sheet-



Section on Line A-B.

Fig. 12

iron nozzle is usually employed. When such an adapter as that shown in Fig. 11 is to be made, it is necessary to use a core composed of three pieces *a*, *b*, and *c*, shown in Fig. 12. In this figure, *b*, which is wedge-shaped, is provided with a handle so that it may be withdrawn and allow the other pieces *a* and *c* to be withdrawn without

Fig. 13

injuring the green retort. The end sections of the core parts are shown in the illustration, also a cross-section through *A B*. The muffle shown in Fig. 13 has an inclined adapter *a* whose front end is closed with an iron reducer on the tile plate, having a hole through it for the escape of fumes.

ZINC REFINING

78. Removal of Mechanically Incorporated Impurities.—Zinc is skimmed after it has been caught in the ladle, and still after being cast it sometimes contains impurities that render it unfit for commercial use, as they exert an injurious influence on the quality of the zinc. These impurities increase and decrease in accordance with the purity of the ores smelted, and as iron and lead are frequent associates of zinc ores, most metallic zinc contains more or less of these metals, which interfere with its commercial values. The removal of the mechanically incorporated impurities presents no great difficulty, for their specific gravity is generally much less than that of zinc. To remove this class of impurities, the crude zinc is melted slowly and allowed to remain in a state of quiet fusion for some time, when the impurities will nearly all rise to the top of the bath and may be skimmed off. The lead and iron form the most difficult problem to contend with, but their influence is not noticed in spelter when used for ordinary commercial purposes. The Bertha zinc, when made from carbonate and silicate ores, contains besides .019 per cent. iron only traces of lead, and is sold as spelter without refining. Recently, the Wetherill magnetic concentrator has been introduced at the Bertha Zinc Company's Delton, Virginia, mines with excellent results.

79. Lead in Zinc.—Lead is the impurity most generally found in zinc. Results vary widely in regard to the extent that lead affects zinc. A quantity amounting to $1\frac{1}{2}$ per cent. of total metal will permit zinc to be rolled into sheets without cracking, but will limit their use for many purposes. With 3 per cent. lead the sheets become softer, show bluish

specks, are gray and rough, and are attacked by acid with greater difficulty. Zinc containing lead may be cast for some purposes, but is not suitable for brass of good quality. For graphical purposes, that is, for etchings, zinc must be pure, otherwise the acids will not attack the zinc uniformly.

80. Iron in Zinc.—Iron is an impurity often found in crude zinc. The percentage of iron in zinc seldom exceeds .2 per cent. and can be diminished by refining to .02 per cent. The effect of 1 per cent. iron is said to make zinc less fluid, more brittle, and of less strength. Zinc can hold at least 4 per cent. iron, as is shown when sheet-iron plates or other materials are galvanized, and it is stated that as much as 7 per cent. iron has been found in zinc taken from the condensers of a distilling furnace. The effect of iron will be shown by the greater ease with which zinc will be dissolved in acids, for the purer the zinc, the more difficult is it to dissolve, especially in masses.

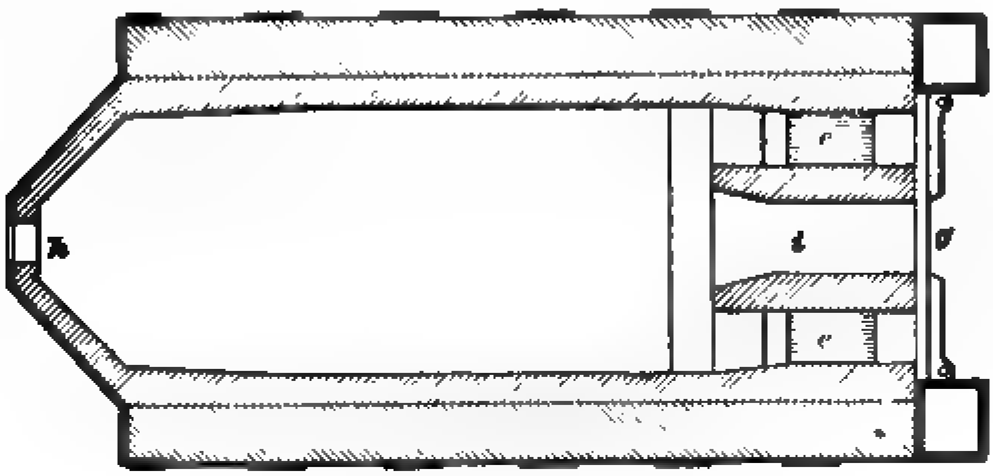
81. Impurities in Zinc.—Arsenic, antimony, bismuth, tin, manganese, magnesium, aluminum, silicon, chlorine, and copper are sometimes found in zinc, but only in very small quantities, so that their effect is scarcely noticeable. The general tendency of the above substances is to harden zinc. Copper and tin, especially, make the zinc so brittle that when it is rolled it will crack at the edges.

82. The chief impurities to be dealt with in zinc refining are lead and iron. The difficulties encountered in this connection are that zinc is much more readily oxidized than either iron or lead, and therefore the removal of the latter in the form of oxides is impossible. Fortunately, both iron and lead can be removed to some extent by the same quiet fusion that is used to separate the mechanical impurities. This depends on the chemical relations existing between the metals, which makes them only slightly soluble in molten zinc. Their solubility decreases with a decrease in the temperature of the fused zinc until the solidifying point is reached.

83. Fusing Lead and Zinc.—If equal parts of lead and zinc are fused together and thoroughly stirred, they will when left quiet separate into two layers, the same as oil and water. This is due to their difference in specific gravity and their small chemical affinity for each other. The lowest layer will be lead, which has a specific gravity of 11.4, and some zinc, while the upper layer will be zinc, which has a specific gravity from 6.8 to 7.3, and some lead in solution. If the temperature be gradually lowered, the amount of each in solution in the other decreases until the solidifying point is reached. The refining of the crude zinc is, therefore, accomplished by fusing it at as low a temperature as possible, with conditions strongly reducing to prevent oxidation of the zinc. The mechanical impurities are skimmed from the surface, while the metal resolves itself into three fairly distinct layers. In cases where both iron and lead are being removed, the heaviest, and therefore the lowest, is lead containing zinc in solution and is entirely fused; the next is the zinc-iron alloy, containing iron in excess, and therefore very imperfectly fusible at the temperature employed; the uppermost and by far the greatest is the refined zinc. From this the metal is ladled into molds, while further amounts of crude zinc are added, thus making the process a continuous one.

84. Refining Furnace.—The zinc obtained from the adapters is cooled and then remelted in a reverberatory furnace constructed especially for the purpose of refining. These furnaces are about 18 feet long and about 9 feet wide. A zinc-refining furnace is shown in Fig. 14 (*a*) and (*b*). In the section, the furnace floor *a* is inclined and made of brick; upon this floor a poor quality of clay *b* is rammed in such a manner as to give the hearth an inclination, dipping towards the flue end and terminating in the well *c*. The bridge wall *d* is made in two sections, one for each grate *e*. The fireboxes are walled off in such a manner as to leave an entrance *i* from the charging door *g* to the hearth. This is necessary because zinc is charged as often as the refined zinc is ladled out of the door *h* at the rear of the furnace.

85. The zinc is melted at the lowest possible temperature, hence the furnace roof is quite high and turns directly into the flue leading to the stack after the flame has passed over the well at the rear of the furnace. By keeping the flame smoky, oxidation is prevented and no impurities are taken up, as might be the case if an iron hearth were used



(a)

(b)

FIG. 14

instead of clay. If an iron rod is slowly lowered into the metallic bath in the furnace, the mass feels soft as far as the molten zinc extends; when the bar reaches the iron-zinc mixture the mass feels hard, somewhat like ice at its melting point. Below this the soft layer of lead is reached.

86. Removal of Impure Zinc. — From time to time the lead is drawn off from the bottom of the well, and after this the zinc-iron, termed *hard zinc*, is removed. There are several methods of removing the lead and impure zinc besides that stated. One consists of a bottomless tube of fireclay, the lower edge of which is notched. It is placed in the furnace before the leady zinc commences to separate and is left in it during the whole operation. The impure zinc passes into the tube from the bottom through the notches and is ladled out from it as soon as it reaches a certain height. The impure bottom zinc is refined by distillation or electrolysis unless it can be sold to silver-lead smelters.

87. The zinc, which after quiet fusion has floated out to the top of the bath, is ladled out into iron molds. After cooling, it is ready for market and is known as *spelter*. The skimmings from the zinc, rich in zinc, known as *zinc ashes*, are added to a rich ore charge in the process of distillation. A considerable portion of zinc can be liquated out of the ashes by dusting over them sal ammoniac before drawing them from the furnace. This operation lessens the quantity of ashes and material that must otherwise be placed with the dross and fume in the upper retorts of the furnace.

MANUFACTURE OF ZINC WHITE

88. Zinc-White Pigment.—In the United States, the pigment known as **zinc white** is produced directly from ores. This is made possible by a peculiar combination of favorable circumstances. The greater proportion of this zinc oxide is made by the New Jersey Zinc Company. In 1899, according to statistics, 25 per cent. of all the zinc produced in the United States was in the form of zinc oxide.

89. Wetherill Furnace.—With the exception of the Bartlett process already described, the furnace generally used for the process is known as the Wetherill furnace. It

consists of an arched chamber with flues and a grate bottom formed of perforated, flat, iron grate bars. The perforations have the shape of truncated cones, with the smaller base uppermost; in this way clogging is avoided. The firebox is air-tight and has connections for a forced draft. Upon this grate a fire is started, the fuel for which must be of such a sort that no smoke or soot is produced. Anthracite coal is the fuel used.

When a thin bed of incandescent coals has been secured, a mixture of anthracite and pure oxidized zinc ore running rather low in zinc is spread upon it. The ores largely used for this purpose are as follows: (1) Franklinite, containing 35 to 40 per cent. iron, 11 to 15 per cent. manganese, 18 to 22 per cent. zinc, and the balance mainly silica SiO_2 and calcium carbonate $CaCo_3$; (2) the middle product of the magnetic concentrators used for recovering the franklinite; this consists of willemite (anhydrous zinc silicate) and the slightly magnetic portion of the gangue and contains about 14 to 24 per cent. of zinc.

90. Zinc-White Manufacture.—Under the influence of the heat and the forced draft, the combustion of the fresh fuel is started, with the effect that the heat and incandescent carbon reduce the zinc to its metallic form and vaporize it. It is at once reoxidized by the excess of air and carbon dioxide and carried with the products of combustion to the flues. The furnaces are built in blocks and connected by means of individual flues to the main flue, which leads first to a tower in which the gases are mixed and any zinc remaining free is oxidized; then the gases, being driven by fans, pass through cooling chambers. Tower and chambers serve the purpose, in addition to those enumerated, of allowing the coarse, mechanically carried dust to settle out, leaving only the zinc oxide in the gases. These are now sufficiently cool to be forced through bags of cotton cloth, which retain the zinc oxide, on the same principle as that used in the Bartlett process when making white-lead-zinc oxide. The white-zinc oxide caught in the bags is shaken out at intervals and is then

ready for compression into barrels as zinc white. The operation of the furnace is continued until the zinc has been removed as completely as possible; the clinker from the treatment of franklinite is then smelted in a blast furnace for spiegeleisen and the remaining zinc is caught as flue dust, which is treated in a Belgian retort furnace for the production of metallic zinc, as previously explained.

LOSS IN DISTILLATION

91. Loss in distillation of zinc is attributed to the following causes, some of which have been touched upon:

1. Absorption of zinc by retorts and filtration of zinc vapor through them into the combustion chamber of the furnace.
2. Breakage of retorts.
3. Escape of uncondensed zinc from the condensers.
4. Undistilled zinc retained by ashes in the retorts.

The loss from the various sources mentioned is seldom less than from 5 to 12½ per cent. of the contents of the ore, or from 10 to 25 per cent. of the metal. This loss does not include the loss due to concentration when preparing the ore for smelting purposes, which will be from 10 to 25 per cent., but the loss which results after 50 per cent. zinc ore has been delivered to the smelter. Some idea of the advancement made in the recovery of zinc is derived from the fact that in good practice losses have decreased from 20 to 10 per cent.

92. Cost of Production.—Competition has required the closest economy to be practiced at zinc-smelting establishments in this country, and as the result of close attention to details the zinc producers have been enabled to export large quantities of ore, oxide, and metal. The cost of production depends on the three following items: (1) The cost of ore; (2) cost of treatment; (3) loss in treatment.

The *cost of ore* varies in every locality where zinc mining is carried on. The rich carbonate and calamine ores of

Virginia require no preliminary treatment, while the ores of Missouri, Kansas, and New Jersey must be concentrated by mechanical means.

Again, carbonate and silicate zinc ores need only to be calcined before treatment, while sulphide ores demand a thorough oxidizing roast.

93. The *cost of treatment* of zinc ores from the time they are delivered at the furnace will depend on the cost of labor, coal, and refractory material at the smelters. These factors will undoubtedly vary at each plant, so that no one example would satisfy all. For instance, in Belgium or Silesia labor is cheaper than at La Salle; however, the cost of fuel is less at the latter place.

In Belgium, the consumption of coal is about 4 tons per ton of zinc produced. In Upper Silesia, the consumption of coal for fuel is about 10 tons per ton of metal produced.

94. The *loss in treatment* will, of course, depend on the care with which the operation is conducted and the care with which retorts are constructed. The loss from breaking retorts it is hard to estimate, but the clay used to replace broken retorts is about 400 pounds per ton of metal produced. The breakage of condensers is also a source of loss in zinc. The average at the Crown Smelter Company's works in Wales is 16.7 broken condensers to each ton of zinc produced. The cost of smelting, including loss of metal in treatment, rents, taxes, interest, depreciation in plant, and all general expenses, was $32.28 per ton of metal produced at Swansea, Wales.

ELECTROMETALLURGY

(PART 1)

PRINCIPLES OF ELECTRICITY

1. Electricity is the name given to that which directly causes all electrical phenomena. Electrical science is founded on the effects produced by the action of certain forces on matter, and all knowledge of the science is deduced from these effects.

For convenience and for practical reasons, the study of electricity is divided into two parts, **static electricity** and **current electricity.**

2. Static electricity resides as changes on the surface of non-conducting substances and is excited by friction, contact of two dissimilar substances, and other causes. The *quantity* of electricity in a static charge is exceedingly small, but it is at an enormous tension or high potential. For electrolytic purposes, this branch of electrical science need not be considered.

3. Current electricity is that which flows through conducting substances. The quantity of current electricity may be large and the tension or potential very small. Current electricity is generated by chemical action, by the action of heat, and by disturbances of the magnetic field, as in dynamos.

The study of the phenomena of current electricity is known as *electrodynamics.*

4. Certain substances do not readily **conduct** electricity; that is, they are **opposed to,** or **resist,** the passage of electricity through them. On the other hand, some substances are good conductors; that is, electricity flows more or less freely through them. Substances have accordingly been divided into two classes, termed **conductors** and **non-conductors** of electricity. This distinction is not absolute, for all bodies conduct electricity to some extent, while there is no known substance that does not offer some resistance to its flow.

5. Electrical resistance may be defined as a general property of matter, by virtue of which it *resists* the passage of electricity. Non-conductors, or **insulators,** then, are those bodies that offer an infinitely high **resistance** to the passage of electricity.

6. Conductivity is the facility with which a body transmits electricity, and is the reciprocal, or opposite, of resistance. For instance, copper is of low resistance and high conductivity; wood is of high resistance and low conductivity.

Conductors, then, are substances that offer a comparatively low resistance to the flow of electricity through them.

7. In Table I, various common substances are arranged in the relative order of their non-conductivity. It commences with the most perfect insulators and ends with the best conductors.

TABLE I

RELATIVE NON-CONDUCTIVITY OF SUBSTANCES

1. Ebonite.	10. Silk.	19. Straw.
2. Shellac.	11. Wool.	20. Marble.
3. Caoutchouc.	12. Dry paper.	21. Dry wood.
4. Gutta percha.	13. Leather.	22. Rain water.
5. Amber.	14. Porcelain.	23. Moist earth.
6. Resin.	15. Lime.	24. Charcoal.
7. Sulphur.	16. Dry steam.	25. Brittle metals.
8. Wax.	17. Oil.	26. Ductile metals.
9. Quartz.	18. Dry metallic oxides.	27. Silver.

The difference in insulating power between the extreme ends of the table is very great, in fact beyond comprehension.

8. The relative conducting powers of pure metals and some other substances, according to an eminent electrician, are given in Table II.

TABLE II

RELATIVE CONDUCTIVITY OF METALS

Silver	100.0%	Nickel	13.100%
Copper	99.9%	Tin	12.400%
Gold	77.9%	Lead	8.300%
Aluminum	51.3%	Antimony	4.600%
Zinc	29.0%	Mercury	1.600%
Palladium	18.4%	Graphite	.069%
Platinum	18.0%	Gas coke	.038%
Iron	16.8%		

ELECTRODYNAMICS

POTENTIAL AND CURRENT

9. The term **potential,** as used in electrical science, is analogous with *pressure* in gases, *head* in liquids, and *temperature* in heat. When there is a *difference* of *electrical potential*, an electric current tends to flow *from* the point of higher *to* that of lower potential.

For convenience, it has been arbitrarily assumed and universally adopted that the electrical condition called **positive** is at a higher potential than that called **negative,** and that an electric current flows *from* a positively *to* a negatively electrified body. *An electric current becomes continuous when the difference of potential is constantly maintained.*

VOLTAIC ELECTRICITY

10. The two Italian physicists, *Volta* and *Galvani*, constructed the first so-called **simple voltaic** or **galvanic cell**, shown in Fig. 1. Such an apparatus will develop a continuous current of electricity. It consists essentially of a vessel *A*, containing saline or acidulated water, into which are submerged two plates of dissimilar metals, or one metal *Z* and a substance *C* resembling a metal termed **metalloid.**

FIG. 1

Electrolyte is the name given to the liquid which, as it transmits the current, is decomposed.

A **voltaic battery** is a number of simple voltaic cells properly joined together.

Electrodes, or **poles,** of a cell or battery are metallic terminals attached to the plates *C* and *Z*, Fig. 1, and are used to connect the cell or battery to any exterior conductor or to another cell or battery.

11. Chemical Action in a Simple Cell.—When a piece of ordinary zinc is placed alone in sulphuric acid diluted with water, the zinc is attacked by the acid and a part of it is dissolved into a salt of that metal, called *sulphate of zinc*. At the same time the liquid is decomposed, hydrogen gas is liberated from it, coming up from around the zinc in small bubbles, and the temperature of the whole mass of liquid is raised. If the zinc is absolutely pure, the chemical actions take place more slowly; the bubbles of hydrogen do not immediately rise to the surface, but form around the zinc, protecting it from further action of the acid. By placing another metal in the water, say a piece of copper, and connecting its exposed end with that of the zinc by a conductor, the chemical actions become exceedingly vigorous again. Large quantities of hydrogen gas are also liberated,

but instead of the bubbles appearing around the zinc, they form around the copper and come to the surface; the energy which in the former case was expended in heating the liquid now appears in the form of electric energy. Whenever the connection between the exposed ends is broken, all chemical actions cease and remain inactive until the two metals are again connected.

12. In any voltaic cell the positive electrode will be acted on by the electrolyte, and in electrolysis dissolved or else disintegrated, as in the case of carbon. The negative electrode is the other pole and is not attacked. The differences of **electric potential,** however, between different pairs of metals which compose a voltaic couple are not all equal. In Table III, any two of the substances form a voltaic couple and produce a difference of potential when submerged in saline or acidulated water, the one standing first on the list being the *positive* element or plate and any other below it the *negative*. The difference of potential will be greater in proportion to distance between the positions of the two substances in the list.

TABLE III

THE ELECTROMOTIVE SERIES

1. + Sodium.	5. Tin.	9. Gold.
2. Magnesium.	6. Iron.	10. Platinum.
3. Zinc.	7. Copper.	11. – Graphite (carbon).
4. Lead.	8. Silver.	

13. The potential of a current of electricity is comparatively so small that a voltaic battery composed of a large number of cells is not sufficient to produce a spark of more than one or two hundredths of an inch in air, whereas a small electrostatic machine will produce sparks several inches in length. If, however, the *actual quantity* of electricity is measured by its effects in decomposing

water, then the quantity produced by a simple voltaic cell as small as a thimble would give greater results than that from an electrostatic machine with plates 2 or 3 feet in diameter.

14. *The term* **electromotive force,** *usually written* **E. M. F.,** *is employed to denote that which moves or tends to move electricity from one place to another.* An electric current will never flow unless the conducting path is made of conducting material.

15. A **circuit** is a path composed of a conductor, or of several conductors joined together, through which an electric current flows from a given point around the conducting path back again to its starting point.

A circuit is **broken** or **opened** when its conducting elements are disconnected in such manner as to prevent the current from flowing.

A circuit is **closed** or **completed** when its conducting elements are so connected as to allow the current to pass.

The **external circuit** is that part of a circuit which is outside or external to the electric source.

The **internal circuit** is that part of a circuit which is included within the electric source.

In the case of the simple cell, the internal circuit consists of the two metallic plates, or elements, and the liquid, or electrolyte; an external circuit would be a wire or any conductor connecting the free ends of the electrodes together.

16. Divided Circuits.—A circuit divided into two or more branches, each branch transmitting part of the current, is a **divided circuit;** the conductors forming these branches are said to be connected in **parallel** or **multiple arc.** Each branch taken separately is called a **shunt.**

Conductors are said to be connected in **series** when they are so joined as to allow the current to pass through each successively.

17. A number of cells are said to be connected in **multiple arc** or **parallel** when the positive electrodes of all the cells are connected to one main positive conductor and all the negative electrodes are connected to one main negative conductor, as shown in Fig. 2.

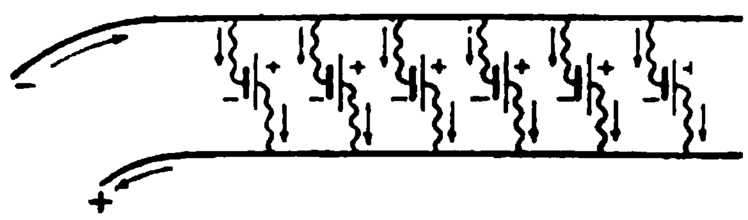


FIG. 2

A number of cells are said to be connected in **series** when the cells are arranged in one circuit by joining the positive electrode of one cell to the negative electrode of the adjacent one, so that the entire current passes successively through each, as shown in Fig. 3.

FIG. 3

When the series and multiple connections are combined, the cells are said to be connected in **multiple series** or **parallel series.** This is accomplished by joining several groups in **multiple** or **parallel,** the cells in each group being connected in **series,** as shown in Fig. 4.

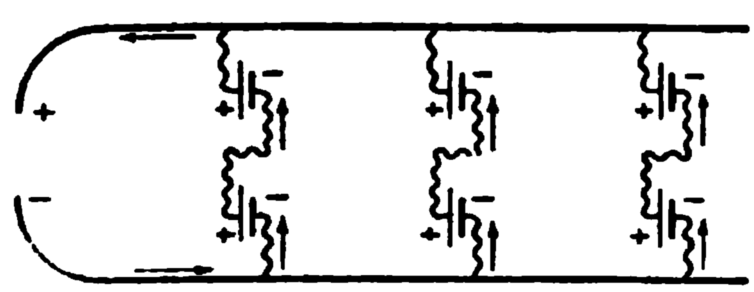


FIG. 4

ELECTRICAL UNITS

18. In every electrical circuit there are particularly three factors, the true relation of which must be clearly understood before they can be measured.

These three factors are:

1. The force tending to move the electricity.

2. The rate of flow of the electricity.

3. The resistance that the force must overcome to produce the flow of electricity.

These factors are respectively termed:

1. The **electromotive force** (written **E. M. F.** or **E.**).

2. The **current** (written C.).

3. The **resistance** (written R.).

In the case of electricity flowing through a conductor, the electromotive force corresponds to the pressure or head of water, and the resistance which a conductor offers to the current corresponds to the friction of the water in pipes. The *strength of an electric current* or the *rate of flow of electricity* is a ratio between the electromotive force and the resistance of the conductor through which the current is flowing. This ratio, as applied to electricity, was first discovered by Dr. G. S. Ohm, and has since been called **Ohm's law.**

19. Ohm's Law.—*The strength of an electric current in any circuit is directly proportional to the electromotive force developed in that circuit and inversely proportional to the resistance of the circuit; i. e., is equal to the quotient arising from dividing the electromotive force by the resistance.*

Ohm's law is usually expressed algebraically, thus:

$$\text{Strength of current} = \frac{\text{electromotive force}}{\text{resistance}},$$

and may be written, by utilizing the symbols given in Art. **18**,

$$C = \frac{E}{R}.$$

When the values of any two such quantities are known, the third can be readily found; for, by transposing,

$$E = C\,R \text{ and } R = \frac{E}{C}.$$

Before giving examples of the application of Ohm's law, the value and significance of some of the various units will be explained. There are two principal systems of units employed in electrical science. They are, respectively, the **fundamental units** and the **practical units**; the latter only will be discussed here.

20. The Ampere.—The practical unit of electric current is the **ampere**. The strength of an electric current is the *rate* of flow of electricity per second and is analogous in expression to the rate of flow of liquids in gallons per minute. When one *practical unit quantity of electricity* is flowing every second continuously, then the rate of flow or the strength of the current is 1 *ampere*. It makes no difference in the number of amperes whether the current flows for a long period or for only a fraction of a second; if the quantity of electricity that would flow in 1 second is the same in both cases, then the strength of current in *amperes* is the same.

The strength of an electric current is determined directly by the effect it produces, and the actual quantity of electricity which has passed between two points in a certain time is afterwards calculated by multiplying the strength of the current by the time.

The principal effects produced by an electric current are magnetic attractions and repulsions, chemical decomposition and precipitation, and heating and luminous effects. Of these, the two most generally used for measuring are: (1) its action before a magnetic needle and (2) its chemical actions.

21. A current of electricity when passing through water decomposes it into its two elements, *hydrogen* and *oxygen*. The *quantity of water decomposed is proportional to the strength of the current flowing*, and also to the time during which it flows. Consequently, a unit strength of current can be conventionally adopted by agreeing that it is that strength of current which will decompose a certain quantity of water in a certain time, and agreeing furthermore on the quantity of water and the time.

22. To Find the Strength of a Current.—By universal agreement, 1 ampere is that strength of current which will decompose .00009324 gram or .0014388 grain of water in 1 second.

Rule.—*To find the strength of an electric current in amperes by the decomposition of water, divide the weight of*

the quantity of water decomposed by the time in seconds required to decompose it; if the mass of water is expressed in grams, divide the quotient by .00009324; but if expressed in grains, divide by .0014388.

Let W = weight of water decomposed in grams;
w = weight of water decomposed in grains;
t = time in seconds required for decomposition;
C = current in amperes.

Then the strength of the current in amperes is given by the formulas:

$$C = \frac{W}{t \times .00009324}.$$

$$C = \frac{w}{t \times .0014388}.$$

23. Decomposition of Water.—Rule.—*To find the quantity of water which an electric current of a given strength can decompose in a given time, multiply the strength of the current in amperes by the time in seconds during which the current flows; if the quantity of water is to be expressed in grams, multiply the product by .00009324; but if in grains, multiply by .0014388.*

Let q = quantity of water in grams;
q' = quantity of water in grains;
t = time in seconds of current flow;
C = current in amperes.

Then the quantity of water that can be decomposed by a current of C amperes in t seconds is given by the formulas:

$$q = .00009324\, C\, t.$$
$$q' = .0014388\, C\, t.$$

EXAMPLE 1.—The current from a voltaic cell decomposes water at the rate of 1.29492 grains per hour; what is the strength of current in amperes?

SOLUTION.— 1 hour = 3,600 seconds. From the formula, the strength of current

$$C = \frac{1.29492}{3,600 \times .0014388} = .25 \text{ ampere. Ans.}$$

EXAMPLE 2.—Find the number of grains of water decomposed in 3 hours by a current of .6 ampere.

SOLUTION.— 3 hours = 10,800 seconds. From the formula, the quantity of water decomposed

$$g' = .0014388 \times .6 \times 10{,}800 = 9.3234 \text{ grains. Ans.}$$

This method of measuring strength of currents is used occasionally in laboratories in connection with electrolytic work, but not extensively.

24. The Ammeter.—Commercial and portable instruments are devised for measuring the strength of current directly in *amperes* and are called **ampere meters,** or simply *ammeters*. The action of the current flowing through the coils in these instruments causes small magnetic needles or other coils of wire to act against either the tension of springs or against gravitational forces. The majority of ammeters are provided with an index needle, which travels over a scale or dial graduated in divisions, each division representing 1 ampere or fractions or multiples of 1 ampere.

Fig. 5 shows the general form of a standard Weston ammeter used for commercial testing purposes. The strength of the current flowing in a circuit can be measured directly in amperes by opening the circuit at any convenient place and connecting the two ends thus formed to the binding posts p and p'. The direction of the current in the circuit should be determined beforehand, so that it passes *into* the instrument by the binding post marked with the positive (+) sign; otherwise, the index needle will be deflected on the scale in the wrong direction, which is liable to

FIG. 5

damage the instrument and cause error in reading when the current passes through in the proper direction.

25. The Coulomb.—The practical unit of quantity of an electric current is the **coulomb.**

The coulomb may be defined as such a quantity of electricity as would pass in one second through a circuit in which the strength of the current is one ampere.

One coulomb delivered per second, therefore, represents a current of one ampere.

One ampere flowing for one second will deliver one coulomb.

If Q = quantity of electricity in coulombs;
C = strength of current in amperes;
t = time in seconds.

Then, $$Q = C\,t.$$

By transposition, $$C = \frac{Q}{t} \text{ and } t = \frac{Q}{C}.$$

EXAMPLE.—Find the quantity of electricity in coulombs that flows around a circuit in $1\frac{1}{2}$ hours, when the strength of current is 12 amperes.

SOLUTION.—From the formula, the quantity of electricity

$Q = C\,t = 12 \times 1.5$ hours $\times$ 3,600 seconds = 64,800 coulombs. Ans.

26. The Ohm.—The practical unit of resistance is the **ohm,** which is the only unit in electrical measurements for which a material standard can be adopted. As a basis for the measurement of resistance, *Siemens* originally proposed a column of mercury having a height of 100 centimeters and a cross-section of 1 square millimeter at the temperature of 0° C; that is, at the temperature of freezing water. This column of mercury he claimed had a resistance of 1 ohm.

27. The idea of utilizing a column of mercury of 1 square millimeter cross-section at 0° C. as the practical unit of resistance has been universally adopted, but the height of this column has never been exactly determined. There are, therefore, various values of the unit often found quoted. Table IV gives these various values in tabular form with annotations denoting their use.

TABLE IV

VARIOUS VALUES OF THE OHM

Name	Height of Mercury Column	Cross-Section of Mercury Column	Use
Siemens Unit...	100 cm.	1 sq. mm.	Out of use, because incorrect.
British Association Unit, written B. A. U...	104.8 cm.	1 sq. mm.	Out of use, because incorrect.
Legal Ohm (commonly called Ohm)........	106.0 cm.	1 sq. mm.	In all technical measurements and calculations.
International Ohm.........	106.3 cm.	1 sq. mm.	Latest and most exact determination. Correct within $\frac{1}{5000}$ part. Not yet in general use.

28. The relative values of these units are given by the following list:

1 legal ohm	=	1.0112 B. A. U.
1 legal ohm	=	1.0600 Siemens unit.
1 B. A. U.	=	.9889 legal ohm.
1 B. A. U.	=	1.0483 Siemens unit.
1 Siemens unit	=	.9540 B. A. U.
1 Siemens unit	=	.9434 legal ohm.

When the ohm is mentioned in this discussion, it represents the resistance of a column of mercury 106 cm. (or 41.7323 inches) high, having a cross-section of 1 sq. mm. (or .00155 sq. in.) at 0° C. (or 32° F.).

RESISTANCE

29. Resistance is that attribute of a conductor or of a circuit which determines the strength of the electric current that can be sent through the conductor or the circuit, around which a constant difference of potential is maintained, as shown by *Ohm's* law, Art. **19.**

If a given conductor offers a resistance of 2 ohms to a current of 1 ampere, it offers the same amount, no more nor no less, to a current of 10 amperes.

Rule.—*The resistance of a given conductor is always constant at the same temperature, irrespective of the strength of current flowing through it or the electromotive force of the current.*

30. When it is required to find the resistance of a conductor of which the length is varied, though all other conditions remain unchanged, the following formula may be used:

$$r_1 : r_2 = l_1 : l_2, \text{ or } r_2 = \frac{r_1 \times l_2}{l_1}.$$

In this formula,

r_1 = original resistance;
r_2 = required or changed resistance;
l_1 = original length;
l_2 = changed length.

31. In all examples of proportion, the two lengths must be reduced to the same unit.

Rule.—*The resistance of a given conductor increases as the length of the conductor increases; that is, the resistance of a conductor is directly proportional to its length.*

EXAMPLE.—Find the resistance of 1 mile of copper wire, if the resistance of 10 feet of the same wire is .013 ohm.

SOLUTION.— $r_1 = .013$ ohm, $l_1 = 10$ feet, and $l_2 = 1$ mile $= 5,280$ feet. Then, by the above formula, the required resistance will be equal to

$$r_2 = \frac{.013 \times 5,280}{10} = 6.864 \text{ ohms. Ans.}$$

32. If the sectional area of a conductor is increased and other conditions remain unchanged, the resistance of the conductor will be decreased. For instance, if the sectional area be doubled, the resistance is halved, and, conversely, if the sectional area is halved the resistance is doubled. The resistance of a conductor, therefore, grows with decreasing sectional area and diminishes with increasing sectional area. This may be expressed by the general rule:

Rule.—*The resistance of a conductor varies inversely as its sectional area.*

33. The value of the resistance of a conductor for any change in its sectional area may be obtained from the following formula:

$$r_1 : r_2 = a_2 : a_1, \text{ or } r_2 = \frac{r_1 a_1}{a_2}.$$

In this formula,

r_1 = original resistance;
r_2 = required resistance;
a_1 = original sectional area;
a_2 = changed sectional area.

EXAMPLE.—The resistance of a conductor whose sectional area is .025 square inch is .32 ohm; what would be the resistance of the conductor if its sectional area were increased to .125 square inch, other conditions remaining unchanged?

SOLUTION.— $r_1 = .32$ ohm, $a_1 = .025$ square inch, and $a_2 = .125$ square inch. Then, by the above formula, the required resistance

$$r_2 = \frac{.32 \times .025}{.125} = .064 \text{ ohm. Ans.}$$

34. The resistance of a conductor is independent of the shape of its cross-section. If the sectional area is the same

in all cases, the resistances will be the same, other conditions being similar. When comparing the resistances of copper wires of circular cross-section, it is usually simpler to express the copper wire by its diameter than by its area. The sectional area of any circular cross-section is, however, proportional to the square of the diameter, for the sectional area = diameter^2 × .7854.

Hence *the resistance of a conductor of circular cross-section is inversely proportional to the square of its diameter.*

35. The last rule may be written as a proportion or a formula, thus:

$$r_1 : r_2 = d^2 : D^2, \text{ or } r_2 = \frac{r_1 D^2}{d^2}.$$

In this formula,

r_1 = original resistance;
r_2 = required resistance;
D = original diameter;
d = changed diameter.

EXAMPLE.—The resistance of a round copper wire .12 inch in diameter is .64 ohm; find the resistance of the conductor when its diameter is increased to .24 inch, the other conditions remaining unchanged.

SOLUTION.— r_1 = .64 ohm, D = .12 inch, and d = .24 inch.
Then, by the formula, the required resistance

$$r_2 = \frac{.64 \times .12^2}{.24^2} = .16 \text{ ohm. Ans.}$$

36. The Rheostat.—An apparatus called a **resistance box** or **rheostat** is largely used for reducing or controlling the strength of currents in various circuits. Such rheostats are connected directly in series or shunt with the circuit and are termed *dead resistances*. The resistance in these rheostats is usually made adjustable—that is, the amount of resistance which they offer may be varied at the will of the operator by the use of a sliding contact or by removable plugs. Rheostats in which the amount of resistance is varied by sliding contacts are used mostly where accuracy

is of less importance and where the currents are comparatively large.

Fig. 6 shows a typical form of sliding-contact rheostat. In this particular rheostat, the coils of resistance wire are connected to a row of contact pieces *D*, as shown in the diagram, Fig. 7. The current enters the rheostat through the terminal *A*, passes through the mov-

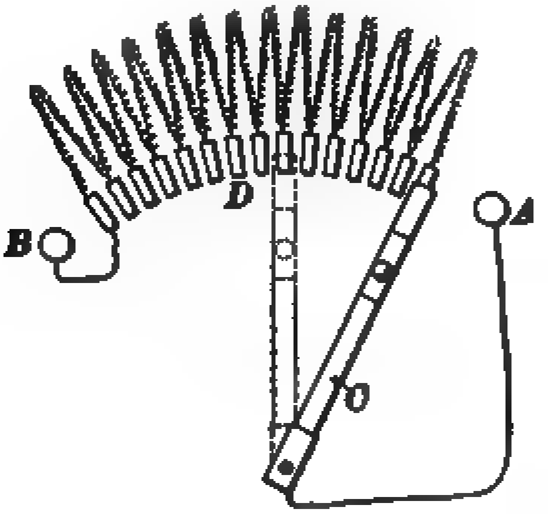


FIG. 6 FIG. 7

able arm *C*, and then through all the resistance coils between the contact piece on which the arm rests and the terminal *B*. When the arm rests upon the first contact piece, as shown by the full lines in this diagram, all of the resistance is said to be *in circuit*—that is, the current passes through all the coils. By moving the arm to the left towards the terminal *B*, as shown by the dotted lines, the coils connected to the contact pieces that have been passed over by the arm are said to be *cut out* of circuit, and the current only passes through the remaining coils.

37. Wheatstone's Bridge.—Electrical resistance may be measured by an apparatus called a **Wheatstone bridge.** A bridge when completed ready for taking measurements consists of three main parts: (1) an adjustable resistance box containing a number of coils, the exact resistance of each coil being known; (2) a galvanometer for detecting

small currents; (3) a battery of several cells. The coils of the resistance box are divided into three groups, two of which are called **proportional** or **balance arms**, and the third is known as the **adjustable arm.** Each proportional arm is composed of three and sometimes four coils of 1, 10, 100, and 1,000 ohms resistance, respectively. The adjustable arm contains a large number of coils ranging from .1 ohm up to 10,000 ohms.

The operation of the bridge depends on the principle of the relative difference of potential between two points in a divided circuit of two branches. The electrical connections of the bridge are shown in the diagram, Fig. 8. *M* represents

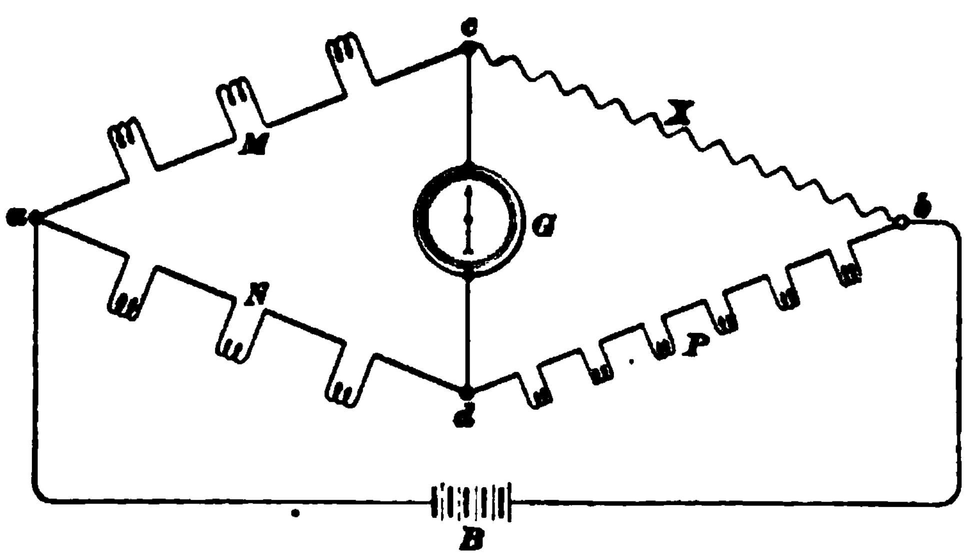


FIG. 8

the resistance of one of the balance arms, which will be termed for convenience the *upper* balance arm; *N* represents the resistance of the other balance arm, which will be termed the *lower* balance arm; *P* represents the resistance of the adjustable arm; and *X* represents an unknown resistance, the value of which is to be determined. One terminal of the detecting galvanometer *G* is connected at *c*—the junction of the upper balance arm and the unknown resistance; the other terminal is connected at *d*—the junction of the lower balance arm and the adjustable arm. One pole of the battery is connected at *a*—the junction of the two balance arms; the other pole at *b*—the junction of the adjustable resistance and the unknown resistance. The current from the battery divides at *a*, part of it flowing through resistances *M* and *X* and the rest through *N* and *P*. When the

resistances M, N, P, and X fulfil the proportion $\frac{M}{N} = \frac{X}{P}$, then the two points c and d will have the same potential, and no current will flow through the galvanometer G. Since the resistances of M, N, and P are known, the resistance of X will be given by the fundamental equation $X = \frac{M}{N} \times P$ when the arms are so adjusted as to cause no deflection of the galvanometer. For example, suppose that the two ends of a copper wire are connected to the terminals b and c, and after adjusting the resistance in the arms so that the galvanometer shows no deflection, the resistances of the different arms read as follows: $M = 1$ ohm; $N = 100$ ohm; and $P = 112$ ohms. Then, substituting these values in the fundamental equation, gives $X = \frac{M}{N} \times P = \frac{1}{100} \times 112 = 1.12$ ohms.

38. The resistance of a given conductor changes with the temperature, and also with its physical condition. In all metals the resistance *increases* as the temperature rises; in liquids and carbons the resistance *decreases* as the temperature rises; and in non-conductors the resistance decreases as the temperature rises.

39. A list of the common metals is given in Table V, in the order of their relative resistances, beginning with silver as offering the least resistance. The first column of figures gives the actual resistance in *microhms* (or $\frac{1}{1000000}$ of an ohm) of 1 cubic inch of the corresponding metal at 32° F. or 0° C. By the resistance of 1 cubic inch is meant the resistance of a piece of the conductor the length of which is 1 inch and whose sectional area is 1 square inch. Therefore, the resistance of any conductor of known dimensions, made of one of the metals in the list, can be determined by applying the formulas in Arts. **33** and **35.** The second column of figures gives the relative resistances of the different metals compared with silver. For example, the resistance of mercury is 62.73 times the resistance of silver or the resistance of iron is 6.46 times the resistance of silver.

TABLE V

Name of Metal	Resistance in Microhms of 1 Cu. In. at 32° F.	Relative Resistance
Silver, annealed................	.5921	1.000
Copper, annealed	.6292	1.063
Silver, hard-drawn............	.6433	1.086
Copper, hard-drawn............	.6433	1.086
Gold, annealed.................	.8102	1.369
Gold, hard-drawn..............	.8247	1.393
Aluminum, annealed...........	1.1470	1.935
Zinc, pressed..................	2.2150	3.741
Platinum, annealed	3.5650	6.022
Iron, annealed..................	3.8250	6.460
Nickel, annealed...............	4.9070	8.285
Tin, pressed....................	5.2020	8.784
Lead, pressed..................	7.7280	13.050
German silver.................	8.2400	13.920
Antimony, pressed.............	13.9800	23.600
Mercury	37.1500	62.730
Bismuth, pressed	51.6500	87.230

40. In a simple voltaic cell, the *internal* resistance, that is, the resistance of the two plates and the electrolyte, is of great importance, for it determines the maximum strength of current that can possibly be obtained from the cell. In the common forms of cells, the internal resistance may be excessively large, owing to the resistance of the electrolyte, the relative resistance of ordinary liquids used as electrolytes being from 1 to 20 million times that of the common metals. In liquids, as in all conductors, the resistance increases as the length of the circuit increases and diminishes as its sectional area increases. Consequently, the internal resistance of a cell is reduced by decreasing the distance between the two plates and by increasing their active surfaces.

The internal resistance of the ordinary forms of cells varies from about .2 to 20 ohms.

41. The Volt.—The practical unit of electromotive force, or difference of potential, is the **volt.** *The volt may be further defined as being that E. M. F. which will cause a current of one ampere to flow against the resistance of one ohm.*

The various terms **electromotive force, pressure, difference of potential,** and **voltage** are, in general, used to signify the same thing—namely, that force which tends to move a current of electricity against the resistance of a conductor.

42. The determination of the value of the E. M. F. in any circuit is made by applying Ohm's law (see Art. **19**), which gives the E. M. F. accurately when the resistance and current are known.

Measuring instruments called **voltmeters** have been devised for indicating electromotive forces and differences of potential directly in volts. Typical of these is the *Weston* voltmeter.

43. Voltmeter.—The **Weston** voltmeter is based on the same principles as the Weston ammeter, and in appearance, Fig. 9, is quite similar. Its internal resistance, as in all voltmeters, is exceedingly large; the resistance of a Weston voltmeter for indicating up to 150 volts is about 19,000 ohms, while the resistance of a Weston ammeter, measuring strengths of currents up to 15 amperes, is only .0022 ohm. It will be seen that, owing to the great resistance, the current passing through a voltmeter is exceedingly small. For example, in the instrument described above, when indicating 150 volts, the current,

Fig. 9

by Ohm's law, is only $150 \div 19{,}000 = .0079$ ampere. All voltmeters are provided with at least two terminals, or binding posts, such as p and p', Fig. 9. Connections are made by two separate conductors, called *voltmeter leads*, from these binding posts to two points between which the difference of potential, or the electromotive force, is to be measured.

The Weston voltmeters usually have a third binding post p'', which, when used with p', corresponds with a second graduated scale situated directly under the main scale, one division of the upper scale having the value of two lower divisions. The majority of voltmeters are also provided with a contact button b, which, when pressed, closes the circuit and allows the index needle to be deflected by the current. When the pressure upon the button is relaxed, the circuit is opened and the index needle returns to the zero mark.

OHM'S LAW APPLIED TO CLOSED CIRCUITS

44. Ohm's law (Art. **19**) expresses the relation between the three fundamental units, resistance, electrical pressure, and current. If any two of these values are known, the third is found by solving the simple equation of their relation. Before applying this law, however, the following four facts should be carefully noted:

I. *The strength of a current* (C) *is the same in all parts of a closed circuit, except in the case of divided circuits.*

II. *In the case of a divided circuit, the sum of the currents in the separate branches is always equal to the current in the main or undivided circuit.*

III. *The resistance* (R) *is the total resistance of the circuit, that is, the sum of the resistances of the internal circuit and of the external circuit or its equivalent.*

IV. *The electromotive force* (E) *in a closed circuit is the total generated difference of potential in that circuit.*

The law may now be stated by the following rules and formulas :

45. **Rule I.**—*The strength in amperes of a current* (C) *flowing in a closed circuit, when the electromotive force* (E) *and the total resistance* (R) *are known, is found by dividing the electromotive force in volts by the total resistance in ohms ;* that is,

$$\text{Current} = \frac{\text{electromotive force}}{\text{resistance}}, \text{ or } C = \frac{E}{R}.$$

Rule II.—*The total resistance* (R) *in ohms of a closed circuit, when the electromotive force* (E) *and the current* (C) *are known, is found by dividing the electromotive force in volts by the current in amperes ;* that is,

$$\text{Resistance} = \frac{\text{electromotive force}}{\text{current}}, \text{ or } R = \frac{E}{C}.$$

Rule III.—*The total electromotive force* (E) *in volts developed in a closed circuit, when the current* (C) *and the total resistance* (R) *are known, is found by multiplying the current in amperes by the total resistance in ohms ;* that is,

$$\text{Electromotive force} = \text{current} \times \text{resistance, or } E = C\,R.$$

46. The following examples show the application of Ohm's law as given by the formulas of the preceding article.

EXAMPLE 1.—What current can be made flow through a circuit having a resistance of 10 ohms, if an E. M. F. of 100 volts is applied ?

SOLUTION.— $E = 100$; $R = 10$; hence, by the formula, the required current

$$C = \frac{100}{10} = 10 \text{ amperes. Ans.}$$

EXAMPLE 2.—What resistance can be overcome by a current of 50 amperes, if the electromotive force is 500 volts ?

SOLUTION.— $C = 50$; $E = 500$; hence, by the formula, the required resistance

$$R = \frac{500}{50} = 10 \text{ ohms. Ans.}$$

Example 3.—What voltage is required to send a current of 25 amperes through a resistance of 4 ohms?

Solution.— $C = 25$; $R = 4$; hence, by the formula, the required voltage

$$E = 25 \times 4 = 100 \text{ volts. Ans.}$$

DROP OF POTENTIAL

47. Referring again to the flow of water in pipes, the analogies may be tabulated as in Table VI, a careful study of which will do much to assist in understanding what is to follow. The fourth analogy of the table states that the loss of pressure, or E. M. F., due to the resistance of conductor is termed **drop of potential.** This drop may be made clearer by the following.

Let Fig. 10 represent a tank T of water with a horizontal discharge pipe $E\ N$, which is provided with open vertical

Fig. 10

tubes at a, b, c, etc. If the outlet at N is closed, the water in the vertical tubes will rise to the height of the water in the tank; but if the water is allowed to flow freely from the outlet at N, then the height of the water in the tubes will be represented by the inclined line at a', b', c', etc. The *pressure*, or *head*, of the water, which is measured by the height of the water in the tubes, decreases in the direction in which the water is flowing, so that the water which leaves the discharge outlet at N has considerably less pressure than the water entering at E.

TABLE VI

ANALOGIES BETWEEN THE FLOW OF WATER AND ELECTRICITY

	Water in Pipes	Electricity in Conductors
I.	Difference of level tends to make water fall from the upper level to the lower level.	Difference of potential tends to make electric current fall from point of high potential to point of low potential.
II.	Difference of level hence acts as a pressure tending to cause a flow.	Difference of potential or E. M. F. hence acts as a pressure tending to cause a flow.
III.	If not entirely obstructed, this pressure actually produces a flow of water.	If not entirely obstructed, this pressure or E. M. F. actually produces a flow of current.
IV.	Some of this pressure is lost by friction of the water against inside walls of pipe.	Some of this pressure is lost by the electrical resistance of the conductor. The loss is called *drop of potential.*
V.	This loss by friction is directly proportional to the length of the pipe, and inversely proportional to the diameter of the pipe.	This loss or drop due to resistance is directly proportional to the length of the conductor and inversely proportional to its area of cross-section.
VI.	No quantity of water can flow through a pipe without suffering some loss in this manner; in other words, there is no such thing as an absolutely frictionless pipe.	No quantity of electricity can flow through a conductor without suffering some loss in this manner; in other words, there is no such thing as an absolutely resistanceless conductor.

48. The same action takes place in a current of electricity flowing along a conductor, and can also be graphically shown. In Fig. 11, B represents a voltaic battery with the *negative* electrode connected directly to the earth at E and the *positive* electrode to a long conductor $A\ L$, which is also connected to the earth at E'. The battery may be regarded

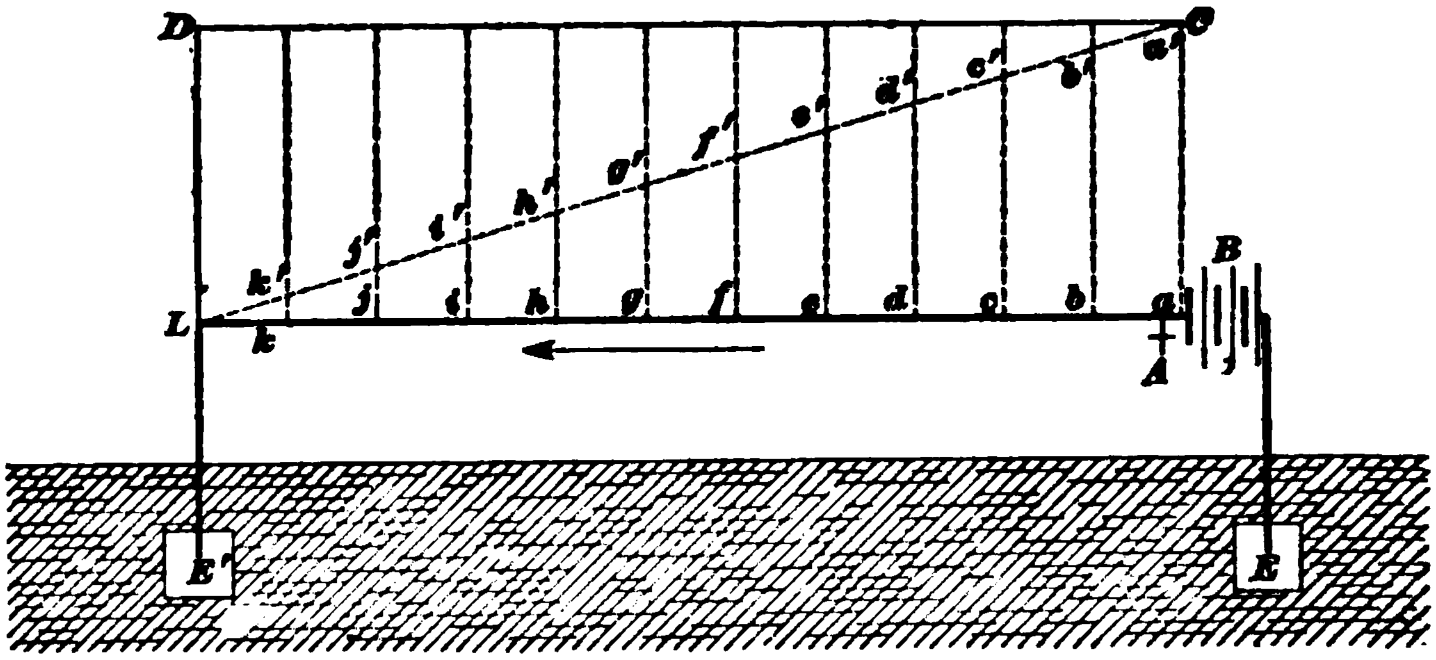


FIG. 11

as a machine which raises the pressure or potential of electricity from zero (or that of the earth) to a height equal to the distance $a\,a'$; or, in other words, the distance $a\,a'$ represents the total *electromotive force* of the battery. If the circuit is *opened* or *broken* between L and E so that no current flows, then the difference of potential between the conductor and the earth is the same at all points along the conductor, and is represented by the distances between the line $C\ D$ and the conductor $A\ L$.

49. When a current is allowed to flow along the conductor, however, the difference of potential between the conductor and the earth *decreases in the direction in which the current is flowing*. The vertical distances $b\,b'$, $c\,c'$, $d\,d'$, etc. represent this difference of potential at the points b, c, d, etc. along the conductor. The *loss* or *drop* of potential is represented by the vertical distances between the inclined line $C\ L$ and the horizontal line $C\ D$. This *loss* or *drop* also represents the difference of potential between the point a and any other point along the conductor. For example, at h

the difference of potential between the conductor at that point and the earth is represented by the distance $h\,h'$; the *loss* or *drop* of potential is represented by the vertical distance between h' and the horizontal line $C\,D$, which distance also *represents the difference of potential existing between the points a and h.*

50. The graphical method of determining the difference of potential is seldom used. Ohm's law not only gives the strength of the current in a closed circuit, but also the difference of potential in volts along that circuit. The difference of potential (E') in volts between any two points along a circuit is equal to the product of the strength of the current (C) in amperes and the resistance (R') in ohms of that part of the circuit between those two points; or, $E' = C\,R'$, which is an example of the use of formula given in Art. **45.** E' also represents the *loss* or *drop* of potential in volts between the two points. If any two of these quantities are known, the third can be readily found; for, by transposing, $C = \frac{E'}{R'}$ and $R' = \frac{E'}{C}$.

51. In a great many cases, it is desirable to have the current flow from the source a long distance to some electric receptive device and return without causing an excessive drop or loss of potential in the conductors leading to and from the two places. In such circuits, the greater part of the total generated electromotive force is expended in the receptive device itself, and only a small fraction of it is lost in the rest of the circuit. Under these conditions, it is customary to decide on a certain drop or loss of potential beforehand, and from that and the current calculate the resistance of the two conductors.

EXAMPLE.—It is desired to transmit a current of 10 amperes to an electrical device situated 1,000 feet from the source; the total generated E. M. F. is 110 volts, and only 5 per cent. of this potential is to be lost in the conductors leading to and from the two points. Find (*a*) the total resistance of the two conductors and (*b*) the resistance per foot of the conductors, assuming each to be 1,000 feet long.

SOLUTION.— 5 per cent. of 110 volts = 110 × .05 = 5.5 volts, which represents the total drop or loss of potential on the two conductors. Let $E' = 5.5$ volts; $C = 10$ amperes; and R' = the total resistance of the two conductors. Then, by formula given in Art. **45**, $R' = \frac{E'}{C} = \frac{5.5}{10} = .55$ ohm. (*a*) Ans. The resistance per foot of the conductor is found by formula given in Art. **30**. In this case, $r_1 = .55$ ohm; $l_1 = 2{,}000$ feet; $l_2 = 1$ foot. Then, the resistance per foot is $r_2 = \frac{.55 \times 1}{2{,}000} = .000275$ ohm. (*b*) Ans.

OHM'S LAW APPLIED TO DERIVED CIRCUITS

52. *A derived or shunt circuit is a branch or additional circuit provided at any part of a circuit through which the current branches or divides, part flowing through the original circuit and part through the new branch.*

A derived circuit is in multiple circuit with the circuit from which it is derived.

In discussing derived or shunt circuits, only that part of the circuit will be considered which is divided into branches, each branch transmitting part of the current; the rest of the circuit is assumed to be closed through some electric source.

Before applying Ohm's law to derived circuits, the meaning of **conductivity** should be thoroughly understood. In Art. **6** it was stated that conductivity is the *inverse* of resistance; or, in other words, it is the *reciprocal* of resistance, that is, $\frac{1}{R}$.

There is no established unit of conductivity; it is used merely as a convenience in calculation.

53. Fig. 12 represents a derived circuit of two branches.

Let r_1 and r_2 = separate resistances of the branches, respectively;

c_1 and c_2 = currents in each branch, respectively;

C = current in the main circuit.

Then, $$c_1 + c_2 = C.$$

When the current flows from a to b, if the resistances r_1 and r_2 are equal, the current will divide equally between the two branches. Thus, if a current of 2 amperes is flowing in the main circuit, 1 ampere will flow through each branch.

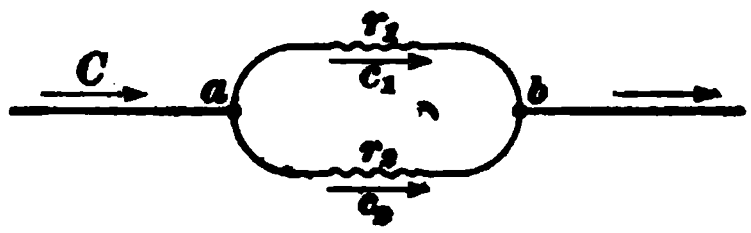


FIG. 12

When the resistances are unequal, the current will divide inversely as the respective resistances of the two branches; or, since the conductivity is the reciprocal of the resistance, *the current will divide in proportion to their respective conductivities.*

In Fig. 12 the conductivities of the two branches are $\frac{1}{r_1}$ and $\frac{1}{r_2}$, respectively.

Therefore,

$$c_1 : c_2 = \frac{1}{r_1} : \frac{1}{r_2}, \text{ or } \frac{c_1}{c_2} = \frac{r_2}{r_1}.$$

EXAMPLE.—Given $C = 60$ amperes; $r_1 = 2$ ohms; $r_2 = 3$ ohms. Find c_1 and c_2.

SOLUTION.— $\frac{c_1}{c_2} = \frac{r_2}{r_1}$, or $\frac{c_1}{c_2} = \frac{3}{2}$, or $c_1 = \frac{3\,c_2}{2}$. But $c_1 + c_2 = 60$, or $c_1 = 60 - c_2$. Substituting for the value of c_1 gives $60 - c_2 = \frac{3\,c_2}{2}$. Transposing gives $5\,c_2 = 120$, or $c_2 = 24$ amperes. Ans. $c_1 = 60 - 24 = 36$ amperes. Ans.

54. It is clear that two conductors in parallel will conduct an electric current more readily than one alone; that is, their *joint* conductivity is greater than either of their separate conductivities taken alone.

Rule.—*If the separate resistances of two conductors are equal, their joint resistance when connected in parallel is one-half of their separate resistance.*

55. When the separate resistances of two conductors in parallel are *unequal*, the determination of their joint resistance when connected in parallel involves some calculation.

In Fig. 12 the conductivities of the branches are $\frac{1}{r_1}$ and $\frac{1}{r_2}$, respectively.

Their joint conductivity $= \frac{1}{r_1} + \frac{1}{r_2} = \frac{r_2 + r_1}{r_1 r_2}$; their joint resistance $R'' = 1 \div \frac{r_2 + r_1}{r_1 r_2} = \frac{r_1 r_2}{r_2 + r_1}$.

Rule.—*The joint resistance of two conductors in parallel is equal to the product of their separate resistances divided by the sum of their separate resistances.*

EXAMPLE.—In Fig. 12, given $r_1 = 4$ ohms, $r_2 = 6$ ohms, and $C = 30$ amperes. Find c_1 and c_2 in the separate branches and the joint resistance of the branches from a to b.

SOLUTION.— $\frac{c_1}{c_2} = \frac{6}{4}$, or $c_1 = \frac{6\,c_2}{4}$. But $c_1 + c_2 = 30$, or $c_1 = 30 - c_2$; substituting, $30 - c_2 = \frac{6\,c_2}{4}$. Reducing gives $10\,c_2 = 120$, or $c_2 = 12$ amperes. Ans. $c_1 = 30 - 12 = 18$ amperes. Ans.

By the above formula, the joint resistance

$$R'' = \frac{r_1 r_2}{r_2 + r_1} = \frac{4 \times 6}{10} = 2.4 \text{ ohms. Ans.}$$

56. In any derived circuit, the **difference of potential** between where the branches divide and where they unite is equal to the product of the sum of the currents in the separate branches and their joint resistance in parallel, as will be apparent from consideration of Ohm's law, Art. **19.**

The **separate currents in the branches** of a derived circuit can be determined by finding the difference of potential between where the branches divide and where they unite, and dividing the result by the separate resistance of each branch.

The **separate resistances of the branches** of a derived circuit can be determined by finding the difference of potential between where the branches divide and where they unite, and dividing the result by the separate currents in each branch.

57. In **practical mechanical work** the unit of time is always 1 minute, and the unit which measures the work

performed in a given time is the **foot-pound per minute.** This unit is called the **unit of mechanical power.**

Power is, therefore, rate of doing work, and hence the power exerted can always be determined by dividing the work done in foot-pounds by the time in minutes required to do it.

58. Equation of Power for Electrical Circuit.—In **practical electrical work,** the unit of time is the **second,** and the unit which measures the work performed in a given time is the **joule per second.** This unit is called the **unit of electrical power,** and has been named the **watt.**

The equation or formula expressing the power exerted in any electrical circuit is determined as follows:

W = total watts exerted in the circuit.
E = volts of electromotive force;
C = current in amperes.

Then, $$W = E\,C.$$

This may be expressed by the following rule:

Rule.—*In every electrical circuit, the power in watts is equal to the product obtained by multiplying the current in amperes by the electromotive force in volts.*

EXAMPLE.—What is the power in watts in an electrical circuit in which .6 ampere flows under a pressure of 110 volts?

SOLUTION.— $C = .6$; $E = 110$; hence, by the formula,
$$W = E\,C = .6 \times 110 = 66 \text{ watts. Ans.}$$

59. When the *power* is to be expressed by the *current and resistance*, the formula is obtained as follows: According to formula in Art. **58,** $W = E\,C$, and according to formula in Art. **45,** $E = C\,R$; substituting this value of $E = C\,R$ in formula $W = E\,C$, then

$$W = C \times C \times R = C^2 R,$$

which may be expressed by the following

Rule.—*In every electrical circuit, the power in watts is equal to the product obtained by multiplying the square of the current strength in amperes by the resistance of the circuit in ohms.*

60. When the *power* is to be expressed by the *electromotive force and resistance*, the formula is obtained as follows: According to formula in Art. **58**, $W = E C$, and, according to formula in Art. **45**, $C = \frac{E}{R}$; substituting this value of $C = \frac{E}{R}$ in formula $W = E C$, then

$$W = \frac{E}{R} \times E = \frac{E^2}{R},$$

which may be expressed by the following

Rule.—*In every electrical circuit, the power in watts is equal to the quotient obtained by dividing the square of the electromotive force in volts by the resistance in ohms.*

ELECTRICAL HORSEPOWER

61. In electrical calculations the **watt** is found too small a unit for practical use; therefore, a unit has been adopted having a value exactly equivalent to the value of the mechanical horsepower. This unit is obtained by transforming 1 horsepower into watts as follows:

1 mechanical horsepower = 33,000 foot-pounds per minute. But 33,000 foot-pounds per minute $= \frac{33,000}{60} = 550$ foot-pounds per second. Hence, 1 horsepower = 550 foot-pounds per second, or 1 foot-pound per second $= \frac{1 \text{ horsepower}}{550}$. And, as 1 joule = .7373 foot-pound, 1 watt = .7373 foot-pound per second, and, hence, 1 foot-pound per second $= \frac{1 \text{ watt}}{.7373}$.

The value of the foot-pound per second is expressed both in horsepower and in watts, so that 1 foot-pound per second $= \frac{1 \text{ horsepower}}{550} = \frac{1 \text{ watt}}{.7373}$, from which we find the value of 1 mechanical horsepower $= \frac{550}{.7373}$ watts = 746 watts. This value, 746 watts, is termed **one electrical horsepower.**

62. The power exerted in any electrical circuit may now be expressed in horsepower units by the following rule:

Rule.—*To express the rate of doing electrical work in horsepower units, find the number of watts and divide the result by 746.*

H. P. = horsepower;
W = watts.

Then,
$$\text{H. P.} = \frac{W}{746}.$$

Since W has the various values given by the preceding formulas, the horsepower may also be expressed by three other equations:

$$\text{H. P.} = \frac{E\,C}{746}.$$

$$\text{H. P.} = \frac{C^2 R}{746}.$$

$$\text{H. P.} = \frac{E^2}{746\,R}.$$

It must be mentioned that a practical unit of electrical power in extended use is the **kilowatt**, having the value of 1,000 watts. This unit is usually written K. W., and is related to the electrical horsepower by the following equations:

1 K. W. = 1,000 watts = 1.34 H. P.
1 H. P. = 746 watts = .746 K. W.

ELECTROLYSIS

63. Historical.—In very early times it was known that often when a bright piece of metal was immersed in a solution of a salt of some other metal, the metal in solution would be deposited upon the surface of the one that was

introduced. When a clean piece of iron was dipped into a solution of copper sulphate $CuSO_4$ or blue vitriol, it immediately became coated with copper, also both copper and iron were coated with silver in the same manner when dipped in a solution of silver nitrate $AgNO_3$. These operations were all very crude, no external source of electricity being employed, the only action being between the metal and the solution.

The first authentic record of electrolysis by the use of a separate discharge was that of Paetz and Van Troostwik. In the year 1790 they succeeded in decomposing water into its constituents, hydrogen and oxygen, by means of electric sparks, using fine gold wires as electrodes. It was not until after the discovery of chemically generated electricity, in 1799, by the Italian physicist Volta, that any really great advances were made in electrolysis. Then, for the first time, it became possible to obtain a continuous current of electricity of considerable quantity and of low electromotive force. Discoveries of new facts now followed one another in rapid succession.

In 1807, Sir Humphry Davy, by means of a powerful voltaic battery, succeeded in decomposing moist potash and obtained metallic potassium at the negative electrode.

The discovery of magneto electricity in 1831, by Faraday, was the mile stone that marked another important turning point in the progress of electrical science. The great cost of electric batteries and the short period of time through which they would last and could be relied on, made experimentation expensive and commercial processes were entirely out of the question.

From Faraday's discovery the modern dynamo has been evolved, so that now by its use electric power can be had at a cost but slightly exceeding that of water and steam power, thus making large operations possible.

At the present day the electrolytic refining of copper has reached such proportions that two-thirds of the total output of copper in the United States is refined by this method.

PRINCIPLES OF ELECTROCHEMICAL ACTION

64. If two dissimilar metals, such as zinc and copper, are placed in an acid or salt solution, such as sodium chloride, no chemical change takes place and both metals are unaffected. Now join the plates together externally, by means of a wire, and the wire is found to be possessed of certain properties which it did not before possess. Briefly, there is an electric current flowing through it which can be recognized and measured by well-known methods, which have been described. If we examine the metals in the solution, we find that so long as the external current is flowing a change is taking place at the surfaces of the two metals, the zinc dissolving and hydrogen being evolved at the surface of the copper, the quantity of each dissolved and evolved element being strictly proportional to the quantity of electricity passing through the wire, although under certain conditions disturbing disorders may be introduced which makes this statement appear not absolutely correct.

65. All cases in which a transformation of energy is involved are, theoretically, if not practically, reversible, and the above-quoted case is no exception to the rule. In other words, if, instead of taking a current out of the arrangement and so dissolving zinc, we put a current into it, then we deposit zinc, and since the amount of zinc dissolved in the first case was proportional to the current taken out, so the amount of zinc deposited in the second case will be proportional to the current put in. This is usually called electrolysis, and in fact involves all the underlying principles of electroplating, electrotyping, electrodeposition, and **electrometallurgy.**

66. What was previously shown to be true of zinc is also true of other metals, and copper, silver, tin, lead, gold, nickel, antimony, iron, mercury, etc. can all be deposited by an electric current from suitable solutions, and in all cases the quantity of metal deposited is strictly proportional to the quantity of the current in amperes multiplied by the length of time which it has been flowing. Not only is this

true, but a simple relation exists between the amount deposited by a given current in a given time and the atomic weights of the elements and is in fact proportional to the atomic weight divided by the *valency*, otherwise called the *chemical equivalent*. For instance, connect four electrolytic vessels in series, the first containing dilute sulphuric acid H_2SO_4 and platinum electrodes; the second a solution of silver cyanide $AgCN$ in potassium cyanide KCN; third, an acidified solution of copper sulphate $CuSO_4$; fourth, a solution of tartrate of antimony in dilüte hydrochloric acid HCl; pass a current of suitable strength through all of these for a definite period of time, and then the quantities of each element liberated at the different electrodes will be proportional to their chemical equivalents. Thus, in No. 1, for every gram of hydrogen H set free at one electrode there will be 8 grams of oxygen O set free at the other $\left(\frac{\text{atomic weight}}{\text{valency}} = \frac{16}{2} = 8\right)$. In No. 2 there will be 108 grams of silver Ag deposited $\left(\frac{\text{atomic weight}}{\text{valency}} = \frac{108}{1} = 108\right)$. In No. 3 there will be 31.5 grams of copper deposited $\left(\frac{\text{atomic weight}}{\text{valency}} = \frac{63}{2} = 31.5\right)$. In No. 4 there will be 40 grams of antimony deposited $\left(\frac{\text{atomic weight}}{\text{valency}} = \frac{120}{3} = 40\right)$.

What has been here shown to be true for the metals which are liberated at the negative electrode is equally true for non-metals, etc. which are liberated at the positive electrode.

67. Faraday's Law.—These two important laws, above illustrated, were discovered by Faraday in 1834, and may be briefly stated as follows:

(*a*) *The quantity of substance decomposed in a given time is proportional to the intensity of the current.* The quantity decomposed by 1 coulomb is called the electrochemical equivalent.

(*b*) *The same current acting at the same time on a series of solutions of various kinds will separate in each solution definite weights of the constituents in the ratio of their chemical equivalents.*

68. Definitions.—Before proceeding further, a few definitions will be necessary.

Electrolysis is the act of decomposing a solution by means of an electric current.

Electrolyte is the solution undergoing electrolysis.

Electrodes are the conductors that lead the current into and out of the electrolyte.

Anode is the **positive electrode,** or the one by which the current enters the electrolyte.

Cathode is the **negative electrode,** or the one by which the current leaves the electrolyte.

Ions are the substances into which the liquid is decomposed.

Anion is the element or ion liberated at the anode, or the electronegative ion.

Cation is the element or ion liberated at the cathode, or the electropositive ion.

69. In Table VII, the substances, their atomic weights, equivalent weights due to valency, and the number of grams per ampere per hour they will deposit are given. The electrochemical equivalent of any element, say gold, is found as follows: The atomic weight is divided by the valency and the quotient multiplied by the number of milligrams of hydrogen that is liberated by an ampere per hour as given in the table.

$$\frac{196.7}{3} = 65.56 \times .037296 = 2.44512.$$

Should the number of ampere-hours be increased, say to 2 or 3, the weight of the substance deposited would be doubled or trebled; consequently, should the number of amperes per hour be increased, the rate of deposition will be increased accordingly.

TABLE VII

ELECTROCHEMICAL EQUIVALENTS OF ELEMENTARY SUBSTANCES

Substance	Atomic Weight	Equivalent Weight	Grams per Ampere per Hour
Aluminum	27.04	9.01	.336030
Antimony	119.60	39.80	1.484300
Bromine	79.76	79.76	2.974700
Cadmium	111.70	55.80	2.079000
Calcium	39.91	19.95	.744480
Carbon	11.97	2.99	.111500
Chlorine	35.37	35.37	1.319150
Cobalt	58.74	29.37	1.095300
Copper	63.18	31.59	1.188100
Fluorine	19.06	19.06	.710860
Gold	196.70	65.56	2.445120
Hydrogen	1.00	1.00	.037296
Iodine	126.54	126.54	4.719400
Iron	55.88	27.94	1.042040
Iron in persalts	....	18.63	.694820
Lead	206.40	103.20	3.846200
Lithium	7.01	7.01	.260820
Magnesium	23.94	11.97	.417410
Manganese	54.80	27.40	1.021900
Mercury	199.80	99.90	3.726360
Nickel	58.56	29.28	1.092020
Nitrogen	14.01	4.67	.174170
Oxygen	15.96	7.98	.298080
Potassium	39.03	39.03	1.455600
Silver	107.66	107.66	4.024800
Sodium	23.00	23.00	.857800
Sulphur	31.98	15.99	.596360
Tin	117.40	58.70	2.189270
Zinc	65.10	32.50	1.212110

70. Voltage Required for Electrodeposition.—In all problems connected with electricity there are two properties of the current to be considered, namely, its quantity and its quality, or, in other words, the number of amperes and the number of volts pressure. In the experiment with the zinc and copper plates, Art. **10**, had a voltmeter been connected across the terminals a deflection of a perfectly definite value would have been obtained, whatever the size of the plates or their distance apart. Now, take the converse of the case, and instead of withdrawing a current from the arrangement put one in; it will then be found impossible to force a current through until the proper voltage has been reached. This is a perfectly definite amount for every element and is intimately connected with its heat of combination or chemical affinity. It is not within the scope of this work to go into the matter, and it may be neglected here with all the greater ease when it is mentioned that it is seldom of practical value. If the voltage for a particular electrolytic arrangement is required, the only way to get a reliable result is to experiment with it in the laboratory. This minimum voltage required to decompose a certain compound in a certain cell is frequently spoken of as its **polarization or back E. M. F.**

71. Polarization of Electrodes. — When an electric current has been passing for a short time between two electrodes immersed in a solution, if the source of current is suddenly switched off and the electrodes instantly connected to a voltmeter, a current is indicated, but in the opposite direction to the original one. This phenomenon, known as **polarization,** is frequently met with in metallurgical operations and may be explained as follows:

The various ions formed at the two electrodes, whether in the solid state, dissolved in solution, or present as gas, adhere to or are absorbed by them and alter their electrical relations. The voltage of this reverse or opposite current has to be overcome before a current can be forced between the electrodes. Polarization not only exists between

different metals, but to a slight extent between different solutions and also between different strengths of the same solution. This latter point becomes of considerable practical importance in copper refining, the solution being stronger at the anode, where it is dissolving copper, and weaker at the cathode, where it is depositing copper. Unless the solution is kept well mixed, there will be a certain amount of polarization between the electrodes.

72. Distinction Between Polarization and Resistance.—Care should be taken not to confuse these two terms. The volts absorbed in an electrolytic cell will be distributed between these two factors, part being used to overcome the ordinary electrical resistance of the circuit, as determined by Ohm's law, and part being used to overcome the polarization. The voltage for the latter purpose will be proportional to the energy required to overcome the affinity of the anion for the cation and which, for a given salt, will be a perfectly definite amount. On the other hand, the ordinary electrical resistance can be reduced to any extent within reason.

73. Electrolytic Separation of Metals.—Every salt has a certain minimum electromotive force at which it is decomposed, and anything less than that does not affect it at all. This obviously gives a method for the separation of two or more metals. Suppose there is a solution containing a mixture of copper and zinc sulphates. It has been determined by experiment and also calculated from the heats of combination that the minimum E. M. F. is lower for copper than for zinc, so that if a current is passed between two electrodes in this solution of a voltage higher than that required for copper, but lower than that required for zinc, then copper alone is deposited on the cathode. When all the copper has been deposited, a fresh cathode may be put in the electrolyte and the voltage raised above that required for zinc, when the zinc will be precipitated. Here, then, is a method for separating two or more metals.

It is not practicable for all metals, however, and in other cases modifications have to be introduced to get a complete separation.

74. Locality of Electrolysis.—The chemical changes directly produced by the current do not take place in the mass or body of the liquid, but at the submerged *surfaces* of the electrodes by which the current enters and leaves the solution, and are strictly limited to the extremely thin layers of metal and liquid in immediate contact with each other.

75. Quality of Electrodeposited Metals.—The physical properties of the electrodeposited substances are largely affected by a number of circumstances, such as the temperature and composition of the electrolyte, the density of the current, i. e., the number of amperes per square inch or per square foot, the rate of deposit, and the condition of the receiving surface. These variations of quality usually refer to the mechanical state and color of the deposited metal. By **reguline** metal is meant that which possesses more or less perfect metallic qualities. **Amorphous** metal is usually in the form of a powder and without crystalline structure. The terms **crystalline, sandy metal, black powder,** etc. are also frequently used to distinguish the appearance of the deposited metals.

76. Black-Powder Deposits.—The circumstance which most affects the quality of the deposited metal is the composition of the electrolyte. The greater number of solutions yield up their metal only in the form of a black powder, however carefully the process be conducted. From only a comparatively few solutions is metal deposited in a reguline state. Copper, antimony, and silver are the easiest to obtain in thick layers, while zinc, gold, platinum, tin, nickel, cadmium, and lead are usually only obtained in thin reguline films, in roughly aggregated nodules or crystalline forms; and most of the other metals can only be obtained in the state of a dark powder.

77. Hardness of Deposits.—Some metals are especially liable to crack and curl up while being deposited. This is particularly the case with antimony, iron, and nickel. Others form very tough and malleable deposits; a deposit of iron or nickel is exceedingly hard. Electrodeposited copper and even gold is frequently remarkably hard. All electrodeposited metals are more or less crystalline and porous and can, therefore, seldom be made to form gas-tight or even water-tight vessels. For this reason, therefore, electrodeposits do not effectually protect the underlying metal. For instance, if steel articles are plated with platinum, it will be found they are still more or less liable to rust, owing to the platinum being more or less porous.

78. Secondary Reactions of Electrolysis.—Very frequently the substances which appear at the electrodes are not those originally set free, but are formed by the action of the originally liberated substance on the liquid or electrode. For instance, if sodium chloride is electrolyzed, chlorine is evolved at the anode and hydrogen and sodium hydrate at the cathode. The chlorine is produced as a direct product of electrolysis, but this is not so with the hydrogen and sodium hydrate. It has been proved beyond doubt that metallic sodium is first deposited, and this then reacts on the water of the electrolyte, forming sodium hydrate and liberating hydrogen.

$$NaCl = \underset{(-)}{Na} + \underset{(+)}{Cl}$$

$$Na + H_2O = NaOH + H.$$

It is the same way in the case of dilute sulphuric acid, which under electrolysis yields hydrogen and oxygen.

79. A number of similar cases are frequently met with in practice. For instance, the ions may react on the electrodes, as when water containing H_2SO_4 is electrolyzed with zinc electrodes, no oxygen being liberated owing to the affinity of the oxygen for the zinc. The ions may be liberated in an abnormal state. Thus, oxygen is frequently

liberated under proper conditions with a variation in its physical condition without change in its chemical condition, as ozone. Hydrogen may be liberated in its "nascent" or uncombined condition when it has peculiarly active chemical properties, as, for instance, its reducing action on nitric acid; thus,

$$HNO_3 + 8H = NH_3 + 3H_2O$$

Hydrogen in the free state will not react in this way.

Metals may be deposited in abnormal conditions. Under certain circumstances, copper may come down in the form of a black powder, antimony in gray masses which possess curious explosive properties.

When a solution of lead is electrolyzed, a deposit of peroxide of lead is formed *on the anode;* thus,

$$\underset{\text{lead nitrate}}{Pb(NO_3)_2} + O + H_2O = \underset{\text{nitric acid}}{2HNO_3} + \underset{\text{lead peroxide}}{PbO_2}$$

Unusual reactions of this sort are frequently met with in electrochemical work

80. Reactions at the Anode.—It has been previously shown that the amount of metal deposited at the cathode was a perfectly definite amount, but it does not follow that the amount dissolved at the anode is equally as definite, particularly if the anode is impure. The amount dissolved is in the case of most metals greater than that deposited, on account of the ordinary chemical action of the solution on the anode which takes place in addition to and independently of the electrolytic action. Besides this, even when a chemically pure anode is used, there is always more or less slime formed upon the surface, which falls to the bottom and makes the loss of weight of the anode apparently even greater. This ordinary chemical reaction frequently takes place at the cathode under certain conditions, although to a much lesser extent than at the anode. It is particularly marked with hot solutions and also strongly acid ones.

81. In the case of depositing a metal from solution, using a soluble anode of the same metal, the theoretical

expenditure of power necessary to carry it over from anode to cathode is nothing. This will be clear from a study of the reactions at the anode and cathode. At the cathode the following reaction takes place, supposing copper to be the metal anode and copper sulphate the electrolyte:

$$\underset{}{CuSO_4} + H_2O = \underset{(-)}{Cu} + H_2SO_4 + \underset{(+)}{O}$$

But at the same time there would occur an oxidation and solution of copper at the anode with a reproduction of the original electrolyte, and therefore a reversal of the former equation; thus,

$$Cu + H_2SO_4 + O = CuSO_4 + H_2O$$

A calculation for the E. M. F. necessary for the reactions indicated by these two equations (it will be seen that one balances the other) is in fact a mere reversal of it, and the resultant is, therefore, zero. What is here shown to be true for copper can be shown to be equally true for many other metals.

82. Resistance of Solutions.—We have seen that in the case of metals, the higher the temperature the greater their resistance. In the case of electrolytes, however, the effect is the reverse of this and an increase of temperature lowers their resistance. Below are given tables showing the effect of heat on various solutions of different specific gravities. The resistance of a solution is also closely associated with its specific gravity, or, in other words, with the amount of salt or acid dissolved in the solutions. Speaking generally, in most cases the resistance is lower the larger the quantity of the substance dissolved. This is true until we get to excessive amounts, as, for instance, in the case of sulphuric acid, where, after a certain point, the addition of more acid causes an increase in resistance. Tables VIII and IX are given below for sulphuric acid and copper sulphate, showing their alteration of resistance with increasing strength of solution and increase of temperature.

83. Table VIII shows the specific electrical resistance of different sulphuric-acid solutions at various temperatures (*Fleeming Jenkin*).

TABLE VIII

Specific Gravity of Acid	Temperatures (Fahrenheit)							
	32°	39.2°	46.4°	53.6°	60.8°	68°	75.2°	82.4°
1.10	1.37	1.17	1.04	.92	.84	.79	.74	.71
1.20	1.33	1.11	.93	.79	.67	.57	.49	.41
1.25	1.31	1.09	.90	.74	.62	.51	.43	.36
1.30	1.36	1.13	.94	.79	.66	.56	.47	.39
1.40	1.69	1.47	1.30	1.16	1.05	.96	.89	.84
1.50	2.74	2.41	2.13	1.89	1.72	1.61	1.32	1.43
1.60	4.32	4.16	3.62	3.11	2.75	2.46	2.21	2.02
1.70	9.41	7.67	6.25	5.12	4.23	3.57	3.07	2.71

84. Table IX shows the specific electrical resistances of different copper-sulphate solutions at various temperatures (*Fleeming Jenkin*).

TABLE IX

No. of Parts of Copper Sulphate Dissolved in 100 Parts of Water	Temperatures (Fahrenheit)						
	57.2°	60.8°	64.4°	68°	75.2°	82.4°	86°
8	45.7	43.7	41.9	40.2	37.1	34.2	32.9
12	36.3	34.9	33.5	32.2	29.9	27.9	27.0
16	31.2	30.0	28.9	27.9	26.1	24.6	24.0
20	28.5	27.5	26.5	25.6	24.1	22.7	22.2
24	26.9	25.9	24.8	23.9	22.2	20.7	20.0
28	24.7	23.4	22.1	21.0	18.8	16.9	16.0

By the term *specific resistance* in the above tables is meant the absolute resistance in ohms of a column of the liquid 1 square centimeter in cross-section and 1 centimeter long; in other words, it is the resistance of a cubic centimeter of

the liquid. The diminution of resistance accompanying a rise of temperature should be especially marked.

85. Theory of Electrolytic Reaction.—Many theories have been brought forward to attempt to explain electrolysis. It is not within the scope of this work to dwell upon these at length, but a simple explanation here introduced may tend to make the matter which follows more clear.

In Fig. 13 is illustrated the effect of electrolysis on hydrochloric acid. Before the current is passed the atoms may be regarded as combined as shown at (*a*). On passing the current the hydrogen atoms next the cathode are deprived of their charge of electricity and so liberated, and the chlorine with which it was previously combined enters into combination with the hydrogen of an adjoining molecule of HCl, the liberated Cl from which combines with the H of the next molecule, and so on until it reaches the anode, where the chlorine is liberated. This would explain the fact that however far the electrodes are apart, the effects of the electrolysis are only seen at their surfaces, the intermediate liquid being apparently unaffected. What applies to hydrochloric acid applies equally well to all electrolytes.

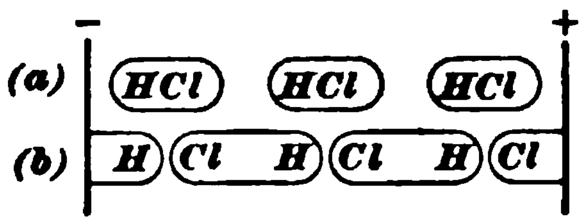


FIG. 13

THEORY OF ELECTROCHEMISTRY

86. The action of the electric current on solutions of various chemical compounds separates them into certain of their constituents, which are liberated at the electrodes In the discussion of the voltaic cell it was shown that by the action of certain salts in solution on two pieces of dissimilar metals the reverse effect was obtained. Instead of an electric current being required to bring about the decomposition of the electrolyte, the salt of the electrolyte acted on the metallic electrodes, one being dissolved, the metal uniting with the acid portion of the salts of the electrolyte. At the other electrode the metal of the salt is set free.

When the two electrodes were joined together externally by a conductor, it was found that an electric current flowed through them. By experiment it has been proved that the quantity of current generated in any voltaic cell is proportional to the amount of chemical decomposition taking place in the electrolyte. To make the operation of an electrolytic cell clear, it may be well to dwell a short time on the theory of dissociation of substances in solution and its relation to electrochemical action.

87. It was observed that solutions of various chemical compounds conducted electricity with greater or less ease, some readily, others with difficulty or not at all. This, of course, required an explanation. After much experimenting and study, physical chemists came to the conclusion that all electrolytes, i. e., solutions which conduct electricity and at the same time undergo decomposition, are in a state of **dissociation,** which means that the constituents of the molecules are in a state of rapid and constant interchange and do not remain firmly fixed in the same molecules. These parts of molecules are termed ions, each molecule being dissociated into two ions. These ions are charged with electricity of opposite kinds, positive or negative, according to their nature, and in all electrolytic actions these ions serve as carriers of electricity from one electrode to the other. A solution of any compound in which the latter does not show this principle of dissociation is a non-conductor of electricity.

88. Conductivity of Electrolytes.—The ions serve as carriers of electricity, and in order to do this they must be in a state of motion, moving from one electrode to the other. Since each ion carries a definite quantity of electricity, it follows *that the conductivity of any solution depends on the number of free ions in it*, or, in other words, on the extent of dissociation. For this reason, solutions of those salts which are completely dissociated are the best conductors. Heat assists greatly in the dissociation of compounds, and consequently the conductivity of electrolytes increases with increase of temperature. Many solid

compounds are non-conductors of electricity at ordinary temperatures, but when heated to a state of fusion become good conductors, the high temperature having brought about dissociation.

89. The Electrodes.—In an electrolyte the positive and negative charges of the ions just balance, so that there is a state of electrical equilibrium, but still each ion retains its own charge. The instant an electric current is passed into the electrolyte through the electrodes a change takes place, one electrode (the anode) becomes charged with positive electricity, while the other (the cathode) becomes charged with negative electricity. In Art. **85** it was shown that particles of matter carrying unlike charges were attached to one another. Bearing this in mind, the action in the electrolytic cell can be more readily understood.

90. Anions and Cations.—The ions of the electrolyte, one kind bearing negative charges and the other positive charges, are, as was previously stated, in an active state of motion and interchange, but still are always in pairs and never free as individuals. When the electrodes become charged, attraction and repulsion take place throughout the solution. The negatively charged ions, called **anions,** move towards the positively charged electrode or anode. The anions next the anode give up their negative charges to the anode, and so are no longer attracted to the positive ions, but are left free. All positive ions, called **cations,** behave in a similar manner, but move towards the opposite or negative electrode, or cathode, where they are set free. Migration of the ions to the poles takes place continually as long as the current is flowing and the supply of electricity is kept up. The ions are never in a chemically free state, except when liberated at the electrodes. They progress through the electrolyte by continually changing places with the ions of the other molecules, ions of the same kind always moving in the same direction. The velocities of the different ions, however, are not always the same, and, as a consequence, the concentration of the electrolyte at the anode may differ

from that at the cathode after the electrolysis has progressed for a time.

91. Strictly speaking, the electric current does not cause the decomposition or dissociation of the electrolyte. This is due to the force and movements of the molecules themselves, which cause the dissociation in their constituents. The current acts simply to separate the ion at the electrodes after the other forces have brought about dissociation.

92. Electrochemical Equivalent.—The first substantial knowledge of the quantitative relation existing between the weights of the ions liberated during electrolysis and the strength of the current required for this liberation is due to the researches of Faraday. His discovery was that equal quantities of electric current did an equal amount of chemical work, i. e., equal quantities of electric current set free chemically equivalent quantities of the ions; or in other words, chemical equivalents of ions have equal electrical capacities. An **electrochemical equivalent** is the weight of that element set free or dissolved and brought into the ionic condition by 1 coulomb of electricity. As an illustration of this consult Table X. The values given are quite accurate, but not strictly exact; however, they serve to illustrate the above point (see also Table VII).

TABLE X

Element	Condition of Salt	At. Wt. $H = 1$	Valence	Electrochemical Equivalents in mg.	No. of Coulombs to Free 1 At. Wt. in mg.
Copper	Cupric	63.18	II	.328587	192.27
Copper	Cuprous	63.18	I	.657175	96.13
Nickel	Nickelous	58.60	II	.305009	192.12
Chromium	Chromic	52.00	III	.180070	288.77
Chromium	Chromous	52.00	II	.270105	192.51
Hydrogen		1.00	I	.010392	96.22
Oxygen		15.96	II	.083872	192.50
Chlorine		35.37	I	.367257	9.30

93. In the above table in the sixth column is given the weight in milligrams of the elements liberated by 1 coulomb necessary to free an atomic weight of the elements expressed in milligrams. It is seen that for all the elements the quantity of electricity necessary for the liberation of the chemical equivalent is the same wherever the valences are the same. For every chemical equivalent of an element in the univalent state there is required approximately 96.25 coulombs for its liberation; for every element in the bivalent state, approximately twice as many coulombs; for every element in the trivalent state, three times as many coulombs are required as when in the univalent state.

From this it appears that the lower the valence of an element in the electrolyte, the less the current required for the liberation of a given weight; thus the *electrochemical equivalent of an element is not a constant factor*, but varies with the state of oxidation or valency of the element in question.

94. Electrochemical Work.—In doing electrochemical work there is another factor that must be taken into consideration, and that is the electromotive force. The electric current is required to do electrochemical work in freeing dissociated ions from other particles. It has been stated that as far as the individual molecules are concerned the ions are not mixed, but they are not free in the sense of being isolated except at the electrodes. They vibrate and exchange partners continually, but the attraction of one another is so great that they cannot be isolated until this affinity or force of attraction is overcome. In the molecule of any substance there is a definite attractive force between the ions. This force varies in different compounds. In Art. **88** it was explained that like ions were capable of carrying charges of electricity of definite quantity. Now, as the electrical work is equal to the product of the current times the electromotive force, it can be seen that the voltage of the current must be high enough to do electrical work sufficient to keep the ions moving steadily towards the electrodes and to separate them from one another as they

are deposited. The theoretical voltage necessary for the electrolysis of any compound can be calculated from its heat of combination, but for practical work in electrometallurgy the proper voltage has been best obtained experimentally, and it is usually higher than the theory calls for.

The foregoing is but a brief resumé of some of the theories of electrochemical action, but it will serve to make some of the points of practical work more clear.

95. Besides the chemical effects of the electrical current in the deposition of metals, there are physical effects which must be taken into consideration. In the electrical deposition of metals, the nature of the deposit at the cathode is of the utmost importance. This is largely dependent on the current used—that is, on the quantity of current per unit area of cathode surface. The nature of the deposit is, however, also dependent on the concentration, composition, and temperature of the electrolyte and on the circulation of the latter at the electrodes. As these factors vary considerably in the treatment of the different metals and solutions, they will be taken up in the description of the special processes *applicable to them.*

96. It is not the object of this work to take up all the applications of electricity to metallurgy, but only the commercially important processes now in use, or those which have great possibilities, both in the treatment of ores or in the refining of impure metals. In the technical portion of the present subject will be discussed the electrolytic treatment of copper, both ores and mattes, and the refining of black and blister copper; the electrolytic refining and deposition of nickel; and the electrolytic refining of silver. Recently there have been a number of electrolytic processes proposed for the metallurgy of zinc and lead, but as yet these have not been developed to such an extent as would warrant more than simple mention of them. Some of them have great possibilities and probably the next few years will witness new and important developments in the electrolytic treatment of these metals.

ELECTROMETALLURGY

(PART 2)

TECHNICAL ELECTROLYSIS

COPPER REFINING

1. Introductory.—The object of the electrolytic refining of copper is twofold: (1) To produce an exceptionally pure metal; (2) to recover the gold, silver, platinum, or other valuable metals that may be alloyed with impure copper. The importance of producing exceptionally pure copper to be used for electric cables and conductors is especially great, since the introduction of the smallest amount of impurity lowers its conductivity enormously. This fact more particularly applies to the presence of arsenic, antimony, bismuth, and silicon, as shown in the following table:

TABLE I

ELECTRICAL CONDUCTIVITY OF COPPER

Copper (pure)	100
Copper containing .216 per cent. of arsenic	61
Copper containing .351 per cent. of arsenic	50
Copper containing .808 per cent. of arsenic	30
Copper containing .206 per cent. of antimony	68
Copper containing .529 per cent. of antimony	56
Copper containing .526 per cent. of silicon	28

2. Ordinary furnace methods are unable to deal with these small quantities of impurities, and it is necessary to look elsewhere for a satisfactory method of eliminating them and recovering the precious metals. The electrolytic method meets the required want and briefly may be described as ordinary copper electroplating on a large scale. If the impure metal is used as an anode and the pure copper as a cathode in a solution of acidified copper sulphate, the impure metal is dissolved when an electric current is passed. Part of the impurities of the metal dissolve into the solution, and part, including the precious metals, fall to the bottom as a muddy residue. Under proper conditions, almost chemically pure copper is deposited at the cathode at approximately the same rate as the impure metal is dissolved.

3. Historical.—The history of the development of electrolytic copper refining is of interest, but not of especial importance, with the single exception of the process invented by J. B. Elkington, which was patented in England in 1865.

This was the first process that refined copper on a commercial scale electrolytically and utilized the current from the dynamo for the purpose. The main features of the process were almost identical with some of those now in use, the difference being mainly in the details of construction and operation of the plant. The ore was smelted and converted into blister copper, which was cast into anode plates about 24 inches long, 8 inches wide, and 1 inch thick. On one end of each plate was attached a T-shaped arrangement of wrought copper, which served to support it in the baths. For the first cathodes, gutta-percha plates covered with bronze powder were used; as soon as a deposit of copper thick enough to be removed was obtained on this, it was stripped from the gutta percha and left in the tank to receive the deposit. Very similar methods are now employed for the preparation of cathodes.

The tanks used were cylindrical fireclay jars about 34 inches deep and 18 inches in diameter. In the bottom

of each jar was a hole, through which the contents could be emptied when necessary, by removing the plug. Each bath was provided with six anodes and four cathodes. The jars were set in rows in a trough inclined so as to allow the electrolyte to flow from one to the other, the solution flowing through pipes connecting the top of one jar with the bottom of the next throughout the series.

The electrolyte (a solution of copper sulphate) was stored in a tank at the head of the system, and after passing through was collected in another tank at the lower end. The electrodes were connected electrically in parallel and the jars in series; the current being supplied by one or more small dynamos. The solution was not allowed to flow steadily, but as soon as that in the baths became impoverished, enough was allowed to flow in to change it throughout the series. The silver and some of the other impurities collected in the bottom of the jars as a sediment, which, when it became too deep, was removed and worked up for silver and gold. The copper obtained was of excellent quality.

This is but a brief description of the process that is the foundation of the modern methods. Since Elkington's process was invented many improvements have been made in the forms of tanks, electrodes, and electrical machinery, and at the same time the scientific side of the subject has been very thoroughly investigated. The most important methods at present in use in the United States will now be taken up in detail.

4. Composition of Copper Before and After Refining.—It is advisable before refining the copper to work it up to a fairly high degree of purity by the ordinary furnace methods, so that the copper contents range from 96 to 99.5 per cent., depending on the nature of the impurities. What is technically known as "blister copper" is frequently used, although it is now becoming more customary to use copper refined by the furnace method. Table II contains the analyses of a sample of converter copper used for anodes and an analysis of the resulting copper deposited on the cathode.

TABLE II

	Lead. Per Cent.	Bismuth. Per Cent.	Antimony. Per Cent.	Arsenic. Per Cent.	Silver Ounces per Ton Per Cent.	Gold Ounces per Ton. Per Cent.
Anode ...	.0103	.0040	.0630	.0211	100.00	.53
Cathode..	.0023	.0005	.0138	.0022	.54	.00

5. The residues from the anodes in the form of mud from the above metal will weigh rather more than $\frac{1}{200}$ part of the copper refined, so that for every 100 tons of anode there will be over $\frac{1}{2}$ ton of residues. These residues will have a composition somewhat like the following:

TABLE III

	Silver. Per Cent.	Gold. Per Cent.	Copper. Per Cent.	Lead. Per Cent.	Bismuth. Per Cent.	Antimony. Per Cent.	Arsenic. Per Cent.
Residues..	53.89	.296	11.01	1.910	3.93	6.25	2.11

A certain amount of impurities would go into solution during the operation of refining. The behavior of these various impurities necessitates the treatment of the solution for the reproduction of pure copper sulphate. The above analyses are merely given as examples and are not to be regarded as necessarily typical. The quantity and quality of residue and the purity of the refined copper are entirely dependent on the composition of the anodes.

SYSTEMS OF COPPER REFINING

6. There are now in use in this country two distinct systems of electrolytic copper refining. These are known as the *multiple* and the *series* systems. Care should be taken not to confuse these terms, which are usually applied to the

arrangement of the electrodes in each individual tank, with the terms series and multiple when used with reference to the connection of the tanks themselves one with the other. Unless otherwise specified, the words *series* and *multiple* will hereafter be used with reference to the arrangement of the electrodes in each individual tank only.

MULTIPLE SYSTEM

7. In the multiple system, which was the method first used for electrolytic refining, the electrodes are alternately arranged so that a positive anode will connect with a negative cathode. The electrodes are suspended in the tank with a clearance of about 1 inch between their edges and the sides

FIG. 1

of the tank and about 6 inches at the bottom, to allow for the residue from the anodes. A section of a multiple tank is shown in Fig. 1. In this figure *a* is the anode and *c* the cathode, both depending from electrical conductors *d* and *e*.

SERIES SYSTEM

8. Before proceeding with a description of the series system, a little preliminary explanation is necessary. Take a tank containing a solution of copper sulphate and provided with an anode and cathode through which a current is

flowing. Now place between the electrodes, but not in any way touching them or otherwise connected to the electric conductors, a sheet of copper and allow it to remain between the anode and cathode for some time, when a certain effect will be observed to have taken place. The side of the copper sheet facing the cathode has dissolved, while that facing the anode has received a coating of copper. Here, then, is the underlying principle of the series method.

A sketch of a series tank is shown in Fig. 2, in which there is one anode *a* at one end of the tank and one cathode *c*

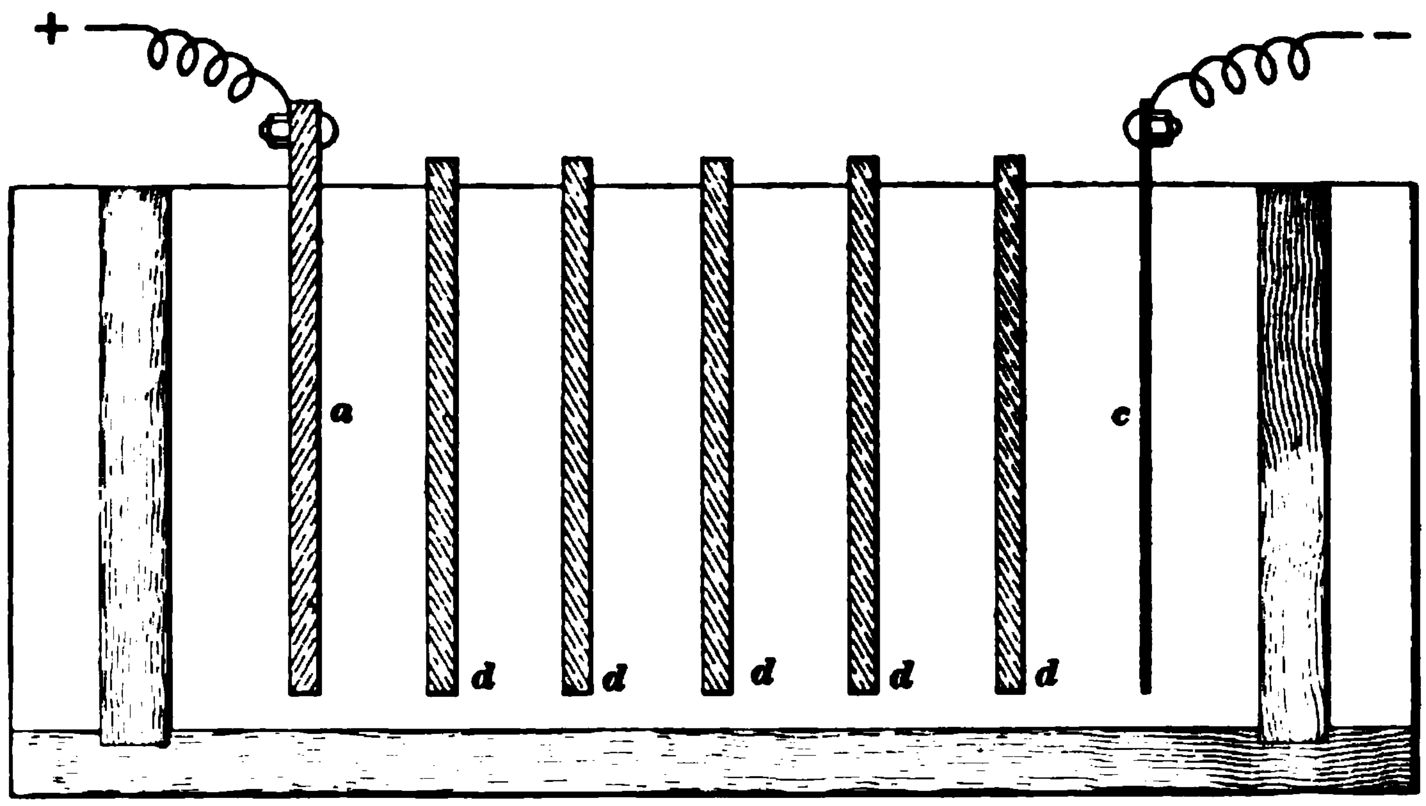


FIG. 2

at the other, the intermediate space being filled with plates *d* of crude metal entirely disconnected from the main conductors and not touching one another. When a current is passed through the cell, each of these plates receives a coating of copper on the side facing the anode, while an equivalent amount goes into the solution on the side facing the cathode. In order to prevent the current getting round the edges of the intermediate plates, and so not performing its maximum amount of work, they are run into fairly tight-fitting grooves in the side of the tank, and the space at the bottom of the tank, which is necessary for the accumulation of residues, is reduced as much as possible. These grooves have the additional advantage of keeping the plates exactly parallel.

The original series method, as described above, is known, after its inventor, as the *Hayden process.* There are a number of so-called variations of this method, but they only differ from the Hayden process and from one another in small details of construction. The principal ones are the *Stallman*, the *Smith*, and the *Randolph*.

9. The Stallman Process.—This process was formerly used at Anaconda, Montana, but was replaced by more efficient methods. Unlike most of the other series processes, it uses cathode plates, the anodes *a* and cathodes *c*, as shown in Fig. 3, being fastened together in couples with an insulating

Fig. 3

medium of glass, asbestos, or some other suitable material between them, as at *d*. At the top, however, electrical connection is made between them either by means of a bolt or by copper-conducting straps; all electrodes are set vertically. The first plate *a* in the tank is an anode; the last one *c* a cathode. Between these are suspended the coupled plates above described. The first anode is connected to the positive and the last cathode to the negative ends of the circuit. The current flows from the anode through the electrolyte to a cathode upon which copper is deposited, then through the metallic connection to the anode of the pair, from whence it passes through the electrolyte to the next cathode, and so on, passing out finally through the last cathode. The arrangement of electrodes is of

doubtful advantage, and the cost of preparing them is necessarily high.

10. The Smith Process.—The principle of this process is very much the same as that of the Stallman process, except that all the plates in the tanks are made of anode copper, except the last one, which is a cathode, and that they are arranged in series, horizontally. The first, or upper, anode is connected with the positive pole of the generator. The current in passing downwards to the cathode passes through a number of intermediate plates, as in the Hayden process, from which it differs by having the plates arranged horizontally instead of vertically.

As the intermediate plates dissolve on the under or anode side, copper is deposited on the upper or cathode side of the next. This continues until the crude metal is all dissolved. Owing to the composition of the anodes, the slimes or mud formed during their solution would fall upon the upper surface of the next layer upon which copper is being deposited, rendering the latter impure. Therefore, cotton or linen diaphragms are stretched between them, upon which the mud is caught. The upper surface of each anode is coated with a thin layer of paraffin and dusted with graphite, to prevent the deposited copper being attacked when the crude metal is dissolved.

There are a number of bad features to this process that make it undesirable. Diaphragms always give more or less trouble. The slimes coat and give them a certain amount of conductivity, thus increasing the danger of short-circuiting. If they get heavily loaded, they may sag and touch the surface of the lower plate and the deposit upon it will enclose part of the cloth and mud, giving a great deal of trouble. As the anodes dissolve away there become fewer contact points with the cathode side of the plate separated by the layer of paraffin. This causes heating and subsequent loss of power. The electrodes, being in a horizontal position, are not accessible to inspection, and if anything goes wrong all of them must be removed in order to locate the difficulty

and correct it. This latter defect is common to all processes using horizontal electrodes.

11. The Randolph Process.—This process is very similar to the Smith, with the current flowing in the opposite direction, i. e., from the bottom to the top, so that the anodes dissolve on their upper sides and the copper is deposited on the under sides of the next plate above. This is a decided advantage, as gravity assists in keeping the slimes away from the depositing copper. Screens, however, may be used to advantage to filter out the very fine mud floating in the solution. Since the solution is richer in copper, and consequently heavier, next to the lower plate, it becomes improverished and lighter at the upper side, where the copper is deposited. On account of this fact and the impurities in it, the solution is liable to stratify. Randolph remedies this defect by causing a good circulation of the electrolyte throughout the tank.

The anodes may be of rolled, pressed, or cast copper. Rolled or pressed copper is to be preferred, as it is more uniform in structure. The anodes are piled in the tanks one above the other and kept from coming in contact by strips or blocks of glass, porcelain, or other non-conducting substance. The bottom plate is connected with the positive pole of the generator and the upper cathode with the negative pole. The plates are made a little shorter than the tank, so that a space is left between them and the walls for the circulation of the electrolyte. The latter flows from the reservoir into the upper part of the tank through a device that delivers it in fine drops. A similar device is used at the outlet where the solution flows to a settling box. In this way a direct electrical connection between the tanks and the vats is prevented, but at the same time allowance is made for an effective circulation.

12. Comparison of the Two Methods.—In discussing the relative value of the multiple and the series system, the points to be considered are: (1) The efficiency of each; (2) the quantity of copper held back in the process; (3) the

relative cost of operation in each case; (4) the relative cost of construction in each case.

13. The Efficiency of Each Method.—In the series system there is a difference of potential (i. e., voltage) of about $\frac{1}{3}$ volt between each plate; so that if, say, 100 intermediate plates are placed between the anode and cathode the total difference of potential is over 33 volts, as against about $\frac{1}{3}$ volt in the multiple system. Of course, the current will be proportionately greater in the latter case, so that the watts (volts $\times$ amperes) will be about equal in both cases. But the voltage being so much higher in the case of the series system, there is an equally greater tendency for leakage to take place either through the layer of mud on the bottom of the tank or through the tanks themselves, which when they are thoroughly saturated with solution become more or less conductive. With reference to the latter point, it is obvious that the tanks must not be lead-lined, otherwise an almost direct short circuit will be established between the anode and cathode at opposite ends of the tank.

A point in favor of the series process is this. If in the series process two plates touch, they are the only ones affected, the rest of the plates in the tank working as usual, whereas if two plates touch in the multiple system, the whole tank is cut out of circuit. This will become clear on reference to Figs. 2 and 3. All things considered, in equally well-managed plants the efficiency of the series system is lower than in the multiple. In either case it is in the neighborhood of 90 per cent. of the theoretically possible output.

14. The Quantity of Copper Held Back in the Process.—The amount of copper in the process represents so much money lying idle on which interest is lost. At first sight this might appear a small matter, but a simple calculation will show that it is not. The multiple process has the advantage here, as under the same conditions only one-half the copper in process is necessary. Advocates of the series process have tried to overcome this difficulty by using thinner plates, and for the purpose of

having them dissolve in a uniform manner they were rolled and consequently more costly to prepare. It is also necessary to change them more often. The relative economy of using thick cast anodes or thin rolled ones is about equal.

TABLE IV

COST PER TON OF CATHODE COPPER

	Multiple System	Series System
Making anodes (including reworking slag)	\$3.40	\$5.57
Fuel at \$4 per ton (for electrolysis)......	3.66	1.73
Consumption of energy in conductors...	.26	.02
Expense involved by loss of efficiency...	.18	.54
Treating residues.....................	.90	.90
Labor (including superintendence)......	3.68	4.14
Interest on \$82,000 and \$62,000, respectively, at 5 per cent..................	.74	.55
Interest on stock of copper in process...	1.41	2.60
Maintenance of plant..................	.76	.97
Oil, waste, light, etc...................	.17	.12
Totals for refining, exclusive of insurance and office expenses..................	15.16	17.14

15. Relative Cost of Operation in Each Case. When the relative cost of operation is considered, the advantage is with the multiple system. Even if the plates of the series system are placed nearer together, there is more liability of the copper "sprouting" and so short-circuiting the plates. Therefore, great care must be exercised to keep the plates parallel, and herein lies another advantage of rolling the plates. But the cost of rolling (and copper must be quite pure before it *can* be rolled) will not be compensated by the voltage saved. There is also more trouble in

stripping the series plates, as the comparatively rough surface gives the deposited copper a grip. The amount of scrap copper is larger in the series system than in the multiple, and the melting down and rerolling or recasting of this all adds to the cost of operation.

16. In Table IV are given figures representing the cost per ton of cathode copper produced in a plant with a daily output of about 15 tons, using steam power and situated where labor and other expenses are not exceptionally high or low.

17. Relative Cost of Construction.—In respect to the relative cost of construction, the series system has slightly the advantage, as the heavy conductors used to carry the large current used in the multiple process are here unnecessary. There is also a saving in the tanks. As it is essential that the tanks be constructed of non-conducting material, the expense of lead lining is saved.

To sum up, it will be seen that although the two systems compare quite favorably with each other, under similar conditions, the multiple system seems to be the more advantageous and the abandonment of the series system in favor of the multiple at several works seems to bear out this statement. Therefore, more attention will be paid to the multiple than to the series system.

CONSTRUCTION OF AN ELECTROLYTIC PLANT

18. Engines and Dynamos.—The subject will now be confined to a closer consideration of the individual parts that together make up an efficient refinery. In selecting engines and dynamos for electrolytic work, one point should be borne in mind. It is of the utmost importance not to stop the operation of a refinery more often or for a longer period than is absolutely necessary, and the engines and dynamos frequently must run 6 months at a stretch. It should be remembered also that during this period they are running practically at full load. Engines and dynamos for

the above reasons should be simple in design and not possess too many moving parts. Allowance should be made in winding the dynamo so that the coils both in the armature and field magnets will not heat up too much and the commutator should be of such a design that it will not give trouble by sparking. In a recent case, where these points had been neglected, after 1 week's run not more than 70 per cent. of the output for which the dynamo was designed could be obtained. A shunt-wound machine should invariably be used, and their price range from $22 to $25 per kilowatt.

The output of the dynamo, that is to say, its voltage and amperage, will, of course, depend on the size of the tanks and their number. It is not unusual, however, to have as high as 180 volts. For preference, a 110-volt machine is used, this being a stock size, since it is a voltage frequently used for lighting and other purposes. Consequently, little trouble is experienced in getting it at short notice, and makers do not have to charge a higher price to cover them for the cost of getting out a special design for a special voltage. If it is desired at any time to sell the machine, it is easier to do so when it is wound for a standard rather than for some irregular voltage.

19. Conductors.—The conductors from the dynamo to the depositing room are made of pure rolled electrolytic copper and are preferably made in strips, so as to expose as great a surface as possible to the cooling action of the air. To economize in conductors, it is advisable to have the refinery as near the dynamo room as possible. When this is the case, the conductors are run at a high-current density, because the amount of energy wasted over such a short distance becomes of less consideration than the initial cost of the conductors. It is quite unnecessary to insulate them with a coating of rubber or the like, but they are fastened to glass insulators and carried overhead on poles. About 1 square inch section of pure copper should be allowed for every 500 amperes a conductor has to carry.

20. Instruments.—An ammeter and voltmeter should always be in circuit. The ammeter is useful for the purpose of seeing whether deposition is going on at the required current density; it shows whether the dynamo is being overloaded or not, and by keeping a record of the average current, the efficiency of the plant can be calculated from the amount of copper theoretically deposited by that current and the amount that is actually deposited. Voltmeters are useful for indicating whether there are any short circuits or defective contacts in the tanks. Any reliable electrical firm can supply satisfactory instruments. A switch is usually placed in the main circuit, not that it is ever used, but merely in case of accident or other emergency. A rheostat is frequently connected in series with the shunt coils of the dynamo for the purpose of regulating the voltage.

21. Tanks.—The first point to be determined is the size of the tanks. From a purely electrolytic point of view it is of course quite immaterial, but there are many points of practical importance. For instance, if it is desirable to save floor space, large and deep tanks are the best; but these have the objection that the electrodes become very unwieldy, and it is more difficult to get them to hang exactly parallel, consequently there is more opportunity for short circuits to occur. However, too many small tanks, while increasing the efficiency of the system, make the first cost excessive. The size that experience has shown to be the best is 2 feet 6 inches wide and 3 feet 8 inches high, inside dimensions, the length depending on the number and distance of the electrodes it is desired to put in. It is not advisable to have them over 6 or 8 feet long.

22. There are several methods of constructing tanks, but the two described are the ones most generally used. Perhaps the better of the two is built of 2-inch pitch-pine plank bolted together and lined with 5- or 6-pound sheet lead. This form of tank has no heavy frame, and the weight of the electrodes is supported directly upon the sides,

as shown in Fig. 4. The other form of tank has a strong wooden frame made of 3" × 4" scantling and is boxed on the sides with 1-inch plank, no bolts being used in the construction. The bottom is made of 2-inch plank nailed to the frame. In this style of tank the framework supports the weight of the electrodes.

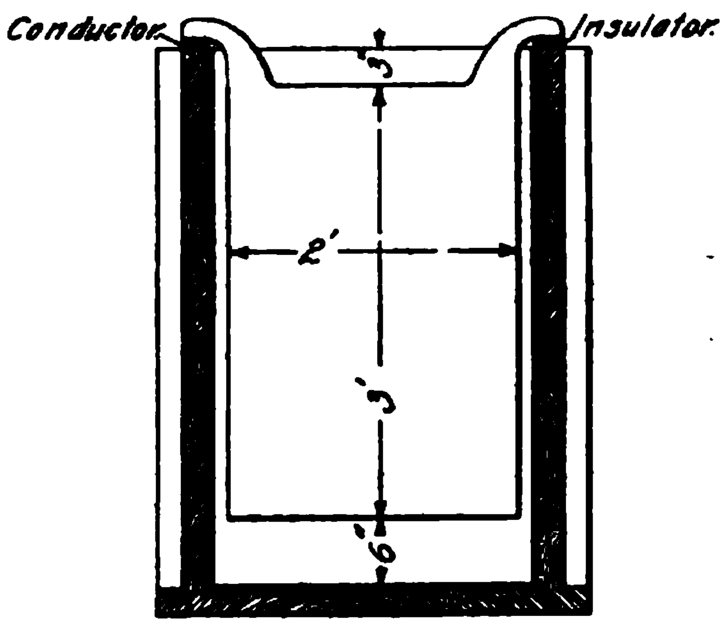


FIG. 4

Lead tank linings are a constant source of trouble, and unless carefully put together are liable to allow leakage of both solution and current. In lining the tanks, therefore, the edges of the lead are melted together by means of the hydrogen blowpipe. To prevent the lead lining from short-circuiting the plates in the event of their coming into contact, it is usual to thoroughly tar the tank inside. To prevent the lining being injured by the sharp corners or projections of the electrodes while lifting them in and out, or in the event of a plate accidentally falling, it is usual, particularly in European refineries, to have a thin lining of match boarding inside the lead.

23. Tank Linings.—In the case of tanks for use in the series process, the lining must be made of some non-conducting material. They are usually made of wood, lined with cement and asphalt. At the works of the Baltimore Copper Smelting and Rolling Company, heavy slate plates coated with tar are used for the Hayden tanks, but these are very expensive.

In European refineries, where manual labor is largely used, the tanks are made rather small, so that the anodes will weigh about 80 pounds, a weight that can be comfortably handled by one man. In the United States, where labor-saving machinery is largely used, there is no practical limit to the weight of the plates from this point of view.

Each tank must be provided with an overflow pipe for the purpose of circulating the electrolyte. The tanks are arranged so that the solution may be drawn from the bottom of one tank and discharged into the top of the next, or else the solution is drawn from the top of each tank and discharged into the bottom of the next, the first system being the more usual. It will be seen that if lead pipe is used for this purpose, a short circuit will be established into the next tank, therefore some non-conducting material, such as glass or rubber, must be used. Of course, the electrolyte itself flowing through the pipes will always constitute an electrical contact between the two tanks, but it is of such comparatively high resistance that it may be neglected. The introduction of this non-conducting pipe is usually done as shown in Fig. 5. At each end and a few inches below the top of each tank is a hole through which the lead lining extends and into which is inserted a piece of heavy glass tubing a, a tight joint being made by a rubber bushing.

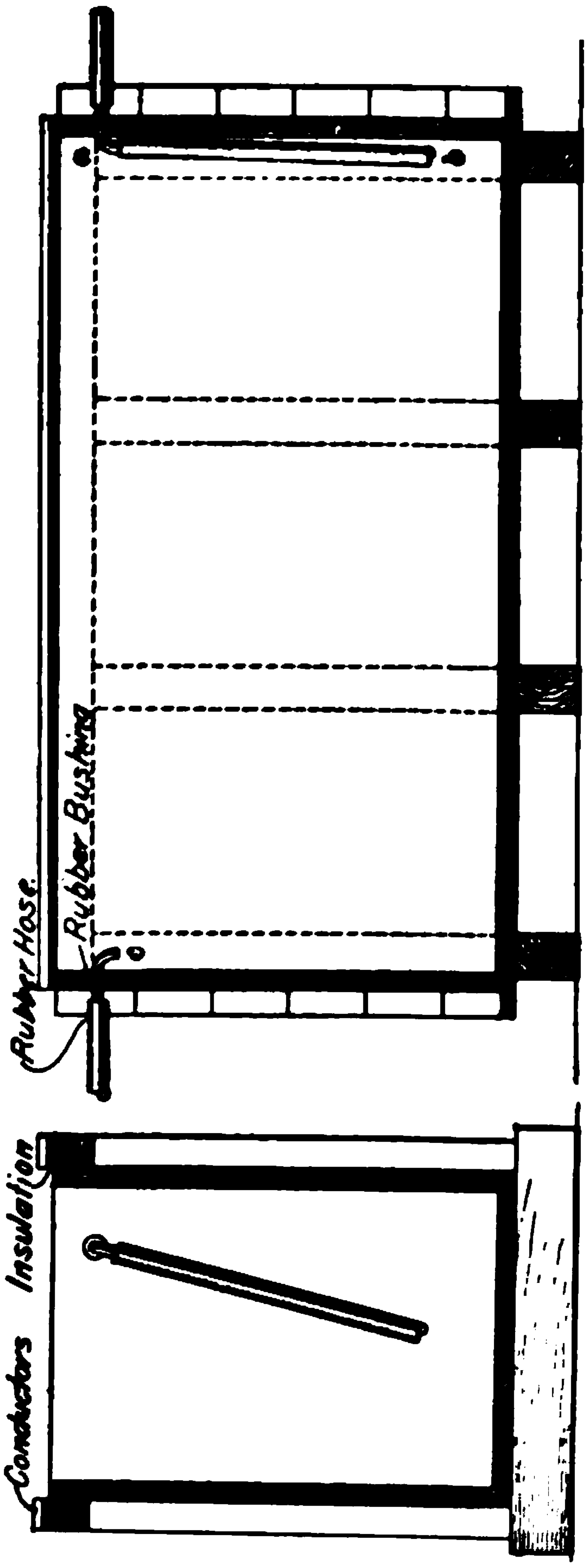


FIG. 5

On the inside, at one end, the glass tube is bent at right angles and a rubber hose b attached, which reaches to within 6 inches of the tank bottom. At the opposite end of the tank another glass tube c is inserted to carry the overflow from the previous tank.

24. Another plan, which has been found very convenient, is to burn a strip of lead in one corner of the tank so as to cut off a triangular portion *a*, Fig. 6. This strip should extend down the tank to within about 6 inches of the bottom. A hole is bored through the wood and lead a few inches from the top of the tank and burned on to the lead lining is a short piece of ¾-inch lead pipe *b* sufficiently long to extend an inch or two beyond the wood. The protruding portion is then trimmed to a conical shape *c* and a piece of vulcanite pipe *d*, which has been smeared on the inside with some rubber cement, is forced on until it is flush with the outside of the tank.

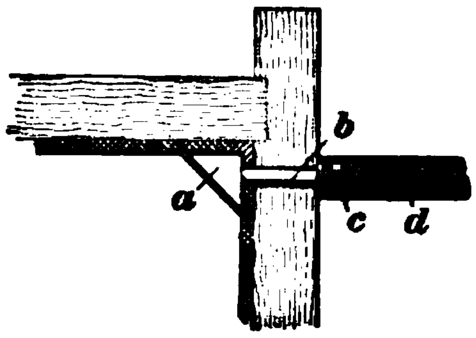


FIG. 6

Another good plan for making joints between lead and glass pipe is to bind fine copper wire around one end of the glass pipe very tightly and then dip this in molten lead. An ordinary wiped joint can be made between this binding and the lead pipe.

25. Anodes.—As previously mentioned, the anodes for the multiple process are usually cast direct from the converter or reverberatory furnace. In the case of the series process, the anodes must be rolled, and to get the copper in a sufficiently malleable condition for this purpose it must undergo a preliminary refining by smelting methods.

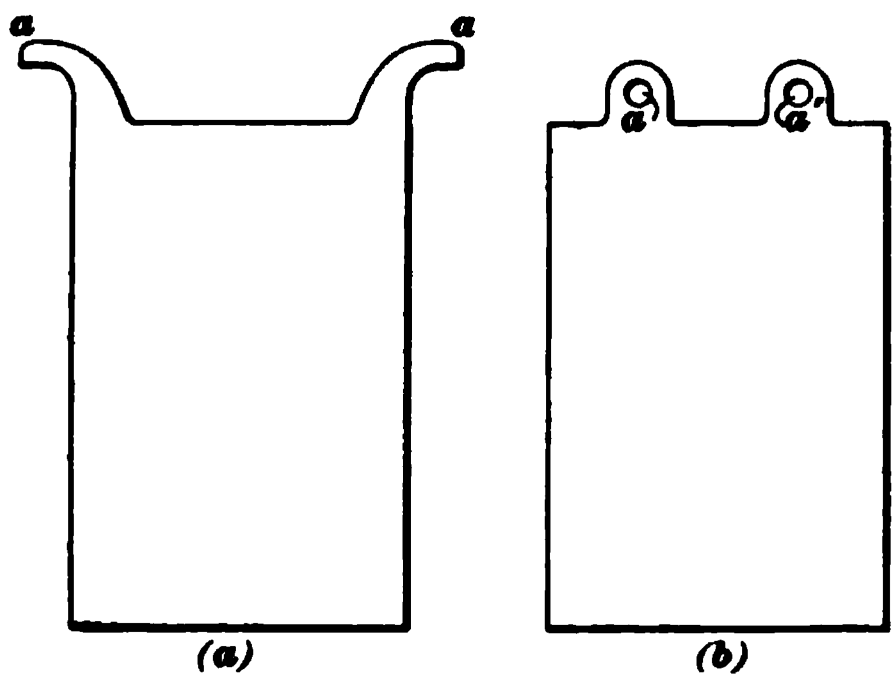


FIG. 7

The most general shape for the anodes is shown in Fig. 7 (*a*), which has an advantage in that no conducting bar is required to suspend it in the vat, as in the case of the cathodes, because the lugs *a* rest on the tank sides; but it also has the

disadvantage of producing a considerable amount of scrap, due to the heavy lugs that must be melted down and recast.

With a view to obviating this trouble, the shape shown in Fig. 7 (*b*) has been used. The anode is suspended by copper hooks passing through the apertures *a* and over a conducting rod placed across the tanks. By this method there are four extra contacts to keep clean.

A recent improvement in the form of a multiple anode is shown in Fig. 8. In this form but one lug *a* is cast upon its upper side. On the opposite side is a hole *b*, into which an iron key *c* is inserted to the depth of 1 inch to support that side. With this mode of suspension the anodes are more likely to hang vertical and parallel with the cathodes and can therefore be placed closer together without danger of short-circuiting. There is also less scrap to remelt than when two lugs are used.

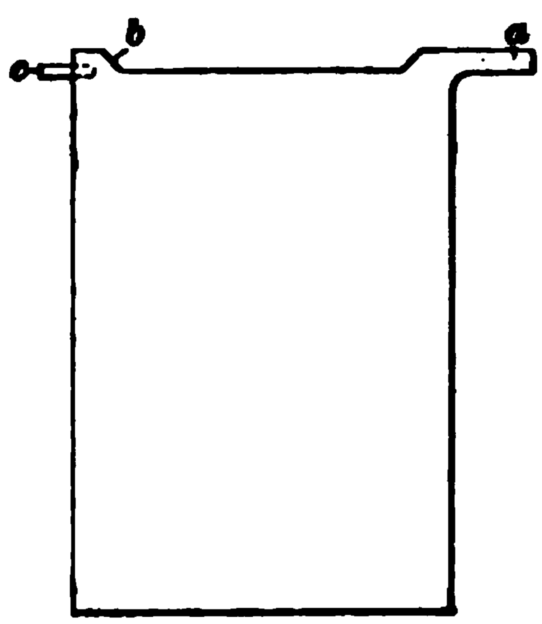


FIG. 8

26. Casting Anodes.—The molds for casting anodes are usually made of cast iron and are placed a little out of the level prior to casting, so that the anodes will be slightly thicker at the top than at the bottom. This is to allow for the greater corrosion that takes place near the surface of the solution. If the anode were made of the same thickness, the top would be corroded before the bottom and the latter would drop into the bottom of the tank, causing short circuits and furnishing additional scrap to be remelted.

Anodes are usually about $\frac{3}{4}$ inch thick and of an area which depends on the size of the tank, that is to say, they are generally $3' \times 2' \times \frac{3}{4}''$, and weigh about 300 pounds. The amount of scrap should not exceed 15 per cent. of the anodes, and every favorable detail should be taken advantage of to reduce the scrap, the recasting of which represents additional expense.

In some refineries the scrap is worked up by having separate tanks in which horizontal lead trays are placed with

the scrap resting on the trays. These are alternated with copper cathodes and the current sent through in the usual way.

27. Cathodes.—The cathodes are made by electrodeposition in the following manner: A certain number of tanks are set aside for making cathodes, in which are placed ordinary rolled-copper sheets about $\frac{3}{16}$ inch thick, the surfaces of which have previously been treated with some material that will prevent the electrodeposited copper sticking. When they have been in the tanks 4 or 5 days, they are removed and stripped, the stripped sheets being sent to the other tanks after straps have been fastened to them by which they may be suspended from the cross conductors. This involves an expense that may be avoided by making the cathodes about 5 inches longer than is necessary for regular tanks, and so produce a sheet of metal sufficiently long to be wrapped around the cross conductors, as shown at *a*, Fig. 9. In order to get for these cathodes a good tough copper that will not break with handling, a current of about 8 amperes per square foot of surface should be used. This will deposit .01 inch per day, and they are usually stripped after 4 days, i. e., when $\frac{1}{25}$ inch thick.

FIG. 9

28. Various methods have been used to prevent the deposited copper sticking, the usual one being to slightly oil the plate and then coat it with a good conducting graphite, after which the edges are dipped for about 1 inch in melted pitch. Some prefer to varnish the surface with weak shellac varnish, mixing about 1 pound of shellac to a gallon of methyl (wood) alcohol. Dipping the plate into a solution of sodium sulphide has also been practiced with some success, as this operation produces a film of copper sulphide.

Sometimes, instead of having separate tanks for making the cathodes, the two outermost cathodes in each vat are

reserved to form new ones. The cathodes are changed when they have acquired a thickness of about ⅝ inch, which in most refineries means about 14 days, so that the cathodes are changed twice as often as the anodes. This is for the purpose of preventing short-circuiting of the tanks due to the copper sprouts on the cathode.

29. Cross Conductors for Cathodes.—These are made of either brass or copper, the most usual shape being shown in Fig. 10 (*a*). One end of the rod has a crowfoot *a*, in order to give it a larger surface of contact with the main conductor. Sometimes, with the object of making the conductor stronger, tubes are used instead of rods.

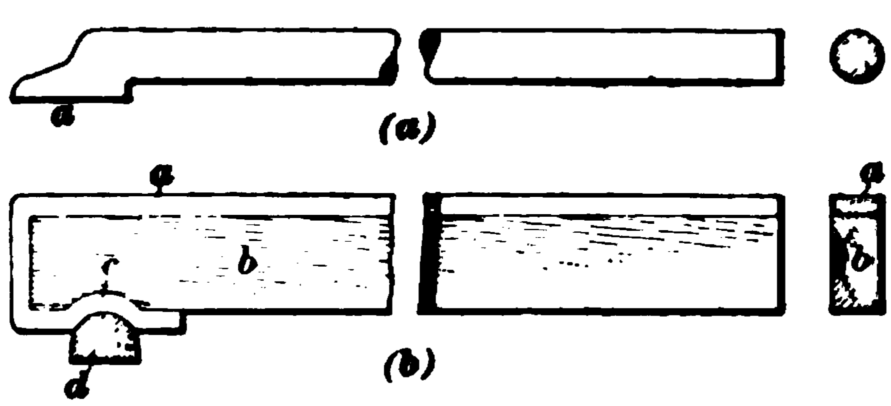


FIG. 10

Brass is used to give the necessary strength, but it has the objection that, compared with copper, it is not a very good conductor. For the purpose of using copper and at the same time maintaining the requisite strength, the form shown in Fig. 10 (*b*) has been successfully applied. The cross-bar *a* is stiffened by wood *b* and is constructed at *c* so as to make a good contact with the main conductor *d*. The semicircular shape of the conductor *d* has a slight advantage by preventing the movement of the cross conductor along its length.

30. Circulation of Electrolyte.—In order to insure a uniform composition to the electrolyte and consequently a regular deposit, it is necessary to keep up a good circulation in the tanks by allowing the solution to flow in at the highest tanks and down through the system, where the overflow is collected in a special reservoir. The solution may be pumped back to the supply reservoir by means of lead or earthenware pumps, or forced up by air pressure, or by means of lead-lined steam injectors. This last method is

open to the objection that the electrolyte is weakened by the condensed steam.

One very ingenious device for the elevation of the electrolyte, operated by compressed air, is shown in Fig. 11.

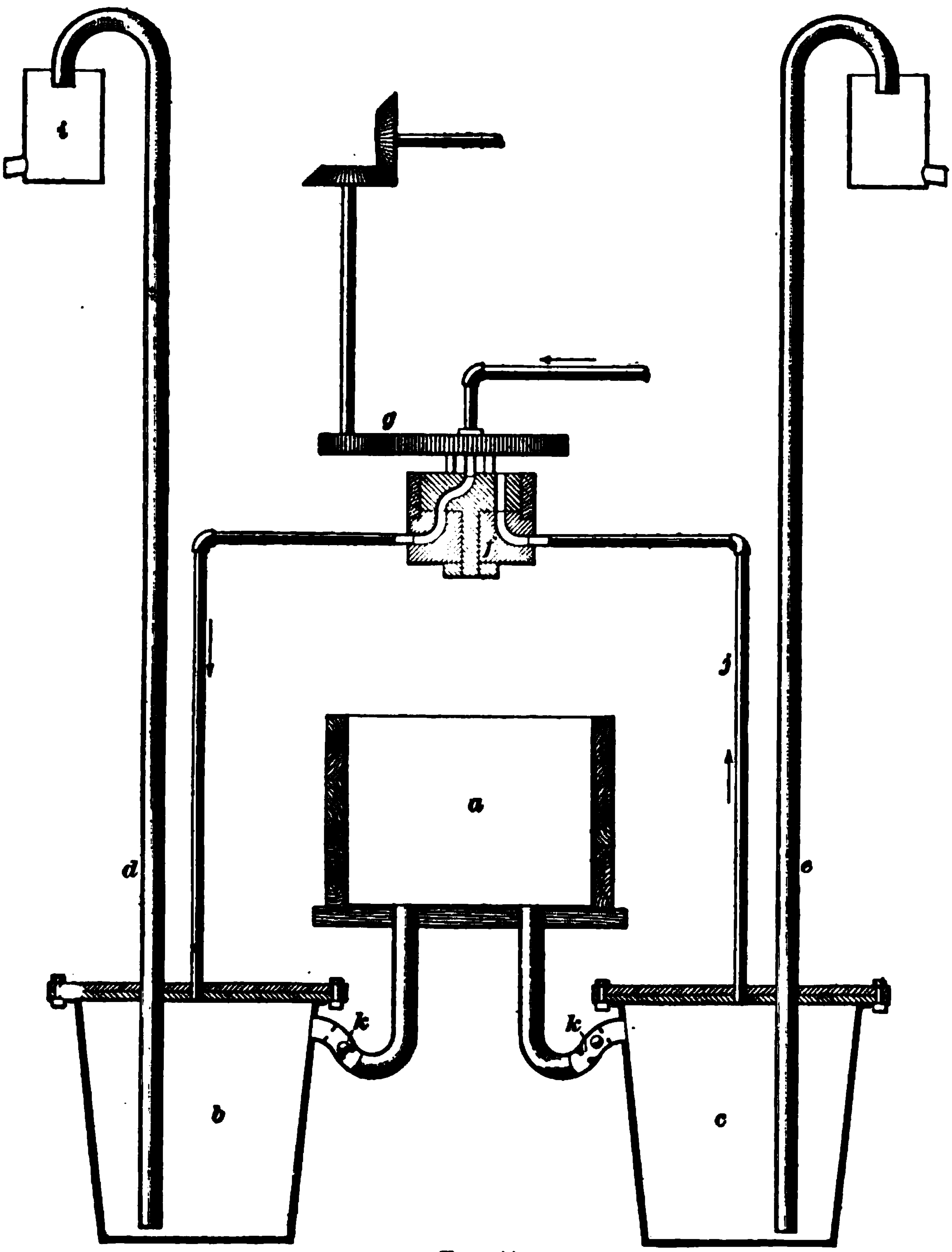


FIG. 11

The electrolyte overflowing from the last tank of the series is collected in the reservoir *a*; the solution flows from *a*

into either *b* or *c* when there is no air pressure in them, the latter being air-tight tanks whose only outlets are through the pipes *d* and *e*. The ball valves *k* prevent any solution flowing back into *a*. Air under pressure passes through the air valve *f*, which is operated by the gear-wheels *g* in such a manner that air flows to *b* during one-half of the revolution and forces solution through *d* into the storage tank *i* at the head of the system. During this part of the revolution the air pipe *j* to *c* is open and, there being no pressure in *c*, the solution can flow into it from *a*. During the second half of the revolution an air pressure is on *c* and *b* is open, so that while one pressure tank is emptying the other is filling. In this way the flow of electrolytes to the head of the system is made continuous. The necessary air pressure for operating this device is provided by a small air compressor.

The agitation or mixing of the electrolyte in the tanks to keep it homogeneous has in some cases been accomplished satisfactorily by introducing jets of air under pressure, which keeps it in constant motion. The air thus supplied not only thoroughly mixes the electrolyte, but has a purifying effect. If care is not exercised, however, this method of agitation is liable to stir up the mud in the bottom of the tank and cause it to adhere to the cathodes.

31. The rate of flow of the electrolyte through the tanks will depend on the amount of impurity in the anode. If the solution is not kept constantly in motion, it becomes stronger in copper and weaker in acid at the bottom, and weaker in copper and stronger in acid at the top.

Take a clear portion of the electrolyte in a tall colorless glass vessel and immerse it in two copper electrodes. Pass through it a strong current for some time, being particularly careful not to disturb the solution. An examination of the solution with the aid of a suitable light will show a stream of heavy liquid descending at the surface of the anode and one of lighter or less color ascending at the cathode.

The most serious consequences that arise from the lack of agitation, however, are those of polarization and the

deposition of impure copper. The former is attended by a direct and great waste of power in evolving oxygen at the anode, and the latter occurs by the deposition of some foreign metal, usually arsenic, bismuth, or antimony, at the cathode. Since the heavier liquid is at the bottom and the liquid is also being withdrawn from the bottom, it will be obvious that a slightly greater "head" will be required on the lighter liquid. This is mentioned so that in erecting tanks due allowance must be made for this by having the discharge at least 2 inches lower than the top of the tank.

32. Connections of Tanks.—Connections with the anodes and cathodes are made as follows: Upon the upper side edges of the tank walls a strip of copper 1½ to 2 inches wide and of such a thickness as is necessary to carry the current without undue heating is fastened, as shown in Fig. 12. On these strips rest the anodes and cathodes. The

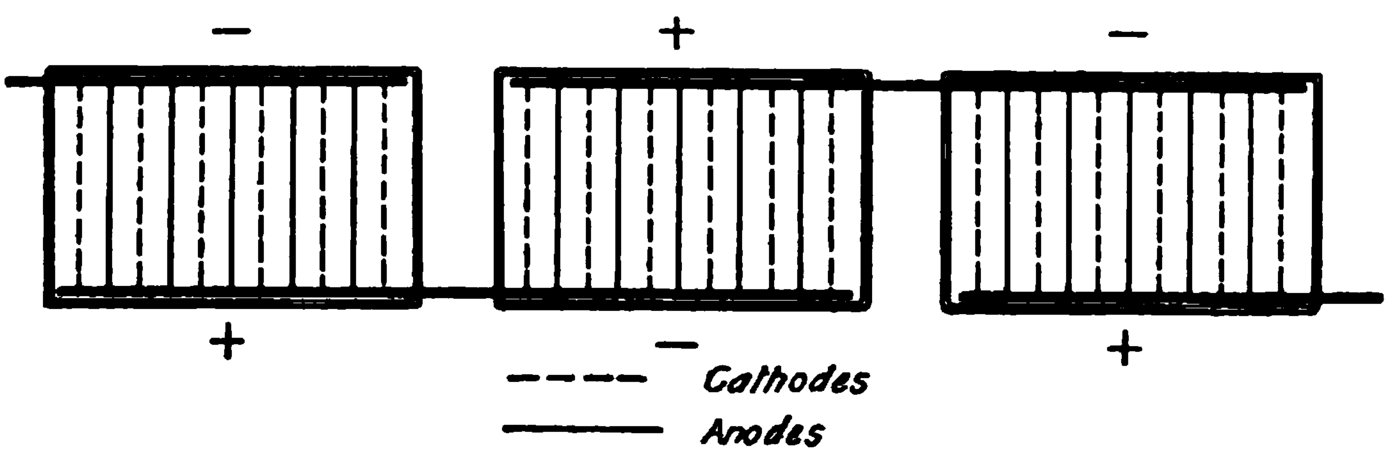


FIG. 12

ends that are not required to make contact at are duly insulated by means of small blocks of wood boiled in paraffin wax or, better still, blocks of glazed earthenware.

In Fig. 13 is shown a good method for the arrangement of the anodes *a*, cathodes *b*, conductors *c*, and insulators *e*; also an economical way of distributing the current. The two outer conductors *c* are of the usual cross-section necessary to carry the current, but economy is introduced by having the middle conductor do for the two tanks; and since the current entirely, or almost entirely, goes straight across to the outside return conductor without going through the middle one, this middle one can be made of much smaller

cross-section than either of the outer ones. Students of electrical engineering will recognize in this another application of the well-known "3-wire" system of distribution.

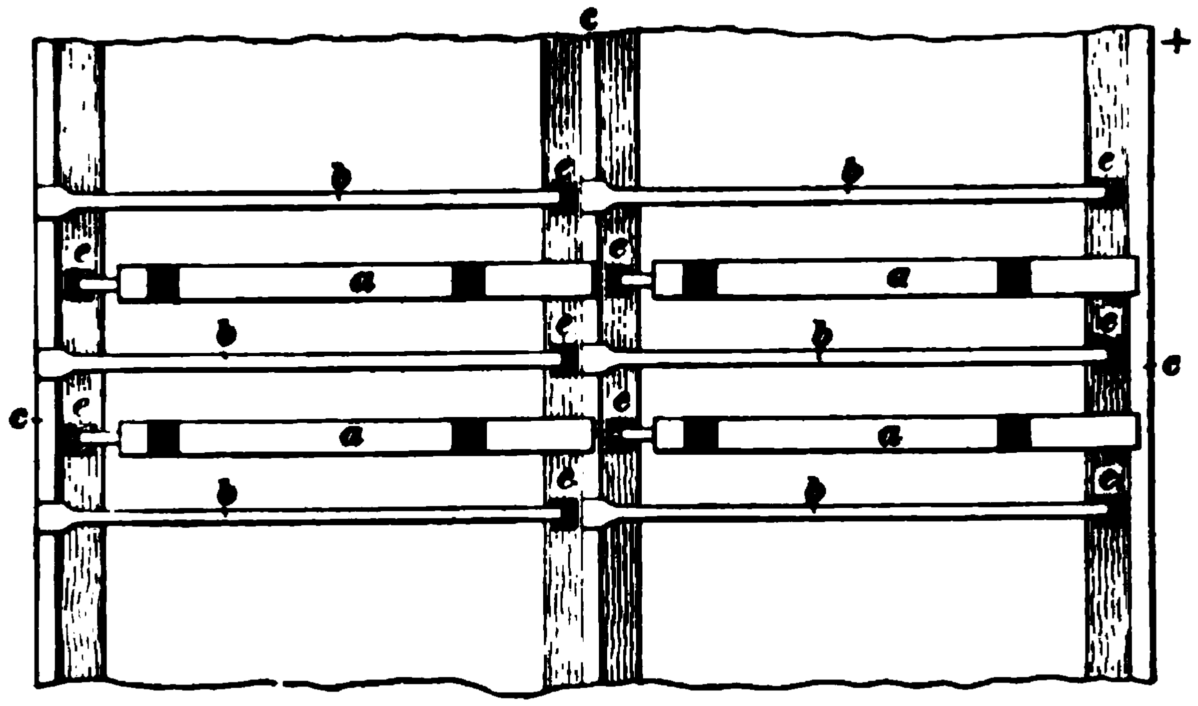


FIG. 13

33. Foundation and Insulation of Tanks.—Owing to the great weight of the tanks, solution, and electrodes, it is easy to see that a thoroughly good foundation is essential. The cell room should be on the ground floor, so that the tanks can rest on a solid base.

As previously mentioned, the tanks are set in "cascade," that is to say, each one is placed a few inches lower than the one before, so as to conveniently circulate the solution. To do this, timbers about 1 foot square are set in concrete, two for each row of tanks, at such an angle as is necessary for the proper arrangement of the cascade. It is hardly possible to use glass insulators, owing to the great weight of their cells. The tanks, therefore, rest on sills that have been coated with a mixture of tar and asphalt. The sills rest on piers of brick, rolled in tar and built up from the beams, or more often the beams are done away with and the piers built up from the floor itself. The whole floor is then asphalted, concreted, or given a coat of tar, and is so sloped that any leakage of solution will drain into a gutter in the center line of the room.

If thought worth while, all leakage, washings, etc., may be caught in a tank and treated for the sake of their copper

contents. A light timber floor is then usually built on the top of this to such a height as will make it most convenient for the men attending the tanks. Should a track for cars be necessary between the rows of tanks, this floor is made in a more substantial manner and the passageways between each two rows of tanks are 3½ to 4 feet wide.

34. Other Details of Construction. — Loading and unloading tanks with anodes and cathodes involves considerable labor. To reduce this to a minimum, above each tank is an overhead crane running on a double track and having on its under side a snatch block and fall. By the aid of this one man can load and unload tanks readily.

Recently, with a view to economizing labor, an arrangement by which a tank can be completely loaded or unloaded at once has been introduced. This is done by having a wooden frame or else a series of iron hooks, by which a whole tankload of anodes and cathodes can be handled at one time.

35. The depositing room should be very dry and well lighted from above. Plenty of ventilation is necessary, so as to keep the air pure. Impure air will play all sorts of mischief with the contacts, and nothing is so detrimental to the satisfactory working of a refinery as dirty contacts. At the same time, the room should be kept at a fairly uniform temperature, and if climatic conditions demand it, heating arrangements should be put in.

PRACTICE OF COPPER REFINING

36. Current Density.—When designing a refinery, one of the most important points for consideration is the current density, that is to say, the number of amperes that will pass for each square foot of cathode surface. As the effect of a variation of current density at the anode is not of much consequence in copper refining, this discussion will be almost entirely confined to the current density at the cathode.

The advantages of using a high current density are that there is less copper in the process; fewer tanks are required; and space is economized. The disadvantages are: The copper is liable to have impurities deposited with it; it has a tendency to be deposited in a less reguline state and is more liable to "sprouting"; it requires a higher voltage per tank and consequently more power for a given output of copper.

37. The exact conditions under which it will be best to work vary in different cases, so that no hard-and-fast rule can be laid down for the best current density, as it ranges from 5 to 20 amperes per square foot, being chiefly influenced by the price of power; the purity of the crude copper and the nature of those impurities; and the required degree of purity of the deposited copper to be produced.

The chief advantage of using a high current density may not at first appear quite obvious, but a calculation will show that under normal conditions there will be a saving by increased output. Now, if it is possible to double the current density without producing injurious effects, the number of tanks, the amount of copper in process, and the size of buildings may be halved and, consequently, there is a saving in first cost and in repairs.

38. Power and Density.—Set off against this is the increased consumption of power due to the increase of current density. This will be seen from the following example: Suppose that there are 200 tanks, the current being 100 amperes and the total resistance .5 ohm. From Ohm's law we have the formula

$$W = C^2 R;$$

W = watts (volts $\times$ amperes);
C = current in amperes;
R = resistance in ohms.

Therefore, in the above example

$$W = (100)^2 \times .5 = 5{,}000 \text{ watts.}$$

Now suppose that the current density is doubled; it is obvious then that only half the number of tanks will be required and that the resistance will, therefore, be halved.

Then, $C = 200;$
$R = .25.$

$$W = C^2R = (200)^2 \times .25 = 10,000 \text{ watts.}$$

It will be seen that the total number of watts consumed will be doubled for the same output of copper. To take another example, suppose that the current is again doubled and the number of tanks again halved.

Then, $C = 400;$
$R = .125.$

$$W = C^2R = (400)^2 \times .125 = 20,000 \text{ watts.}$$

In these calculations polarization is not taken into account at all, but it would not materially alter the relative values of the above figures.

39. The deductions made from the above calculations are that it is more economical to work at a low current density where power is dear, but more economical to work at a high current density and save on interest and capital where power is cheap. This statement is only true under certain conditions, namely, that the impurities in the anode shall be sufficiently small and of such a nature as not to be deposited at the cathode to any appreciable extent. This particularly applies when bismuth, antimony, and arsenic are present, a high current density being more likely to bring these down with the copper than a low one. If the current density is very high, the copper is likely to be in a non-reguline condition, that is to say, it is more or less crystalline and brittle. The majority of refineries run from 8 to 12 amperes per square foot.

40. Distance Between Plates.—Theoretically it is best to have the electrodes quite close together, thereby lessening the resistance. In practice there is a limit to their

nearness in order to prevent short-circuiting. The parallelism between the plates will, in a measure, influence the distance they are to be placed apart, for if the plates are warped or do not hang very nearly parallel, short-circuiting may occur. Small plates are more likely to hang parallel than large ones, and if warped, their smaller size does not allow the warp to be so pronounced.

41. The liability of copper to "sprout" is dependent chiefly on the current density and composition of the solution. It has no doubt been noticed that the copper is invariably thicker and covered with nodules of copper at the edges of the cathode, and that this is the usual source of trouble when short-circuiting takes place. It is important, therefore, to see to what this is due and to check it if possible.

The resistance between opposite points on the electrodes is not equal all over the plates, but is less at the edges, owing to the currrent having room to spread out. The current, and consequently the copper that it deposits, is not distributed equally over the plate surfaces, but takes a course something like that shown in Fig. 14. The current may be made to spread out more evenly over the cathode by making the anode an inch or two smaller than the cathode.

FIG. 14

42. Electromotive Force.—The E. M. F., or voltage, *theoretically* necessary to deposit copper using a pure copper anode is naught, as has been pointed out elsewhere, but actually this is not the case. There is the resistance of the solution to be overcome, since there is a practical limit for the distance between the plates. There is the resistance of the conductors and the numerous contacts of the electrodes that must be overcome, particularly when they get dirty. There are the slimes on the surface of the anode that also

introduce resistance. It is also largely governed by the current density at the cathodes. The difference in composition of the electrolyte at the surfaces of the anode and cathode, owing to incomplete circulation, represents a certain amount of "polarization" that must be overcome. In a badly managed works, where insufficient attention is paid to these matters, the voltage required may be considerable. It is, therefore, impossible to give any general rule that will determine the E. M. F. necessary, but in practice it usually lies between .25 to .6 volt per tank.

43. The Electrolyte.—The composition of the electrolyte varies little in different refineries; the following is about the usual composition: Water, 76 parts; bluestone, 18 parts; 66° Beaumé sulphuric acid, 6 parts. The outside limits appear to be from 15 to 20 per cent. of bluestone and 5 to 6 per cent. of acid. If too much acid is added, oxygen is more liable to be evolved at the anode during electrolysis, thus causing polarization and the consequent waste of energy. If too much bluestone is present, there is a liability for it to crystallize where it is not required—namely, in the tanks or pipes, choking up the latter and giving endless trouble. The temperature of the solution should be kept slightly warm, not hot, say at 70° F., as this will in a meassure prevent crystallization. The warming effect of the current is usually sufficient for this, but if necessary steam should be blown in.

An analysis should be made daily of the electrolyte for copper and sulphuric acid, and periodical tests, say once a week or oftener, should be made for the impurities. Rough tests may be devised for these in some cases so that they can be carried out in a few minutes by the foreman. For instance, if bismuth gives trouble, take a small quantity in a beaker and add a few drops of bromine water. If a white cloud occurs almost instantly, there is too much bismuth present and the electrolyte must be purified. If, however, the cloud takes 10 seconds or more to form, there is no danger as far as bismuth is concerned.

EFFECT OF IMPURITIES IN THE ANODES

44. The impurities in the anodes are after refining distributed in the mud, in the electrolyte, and in the deposited copper. By far the largest amount is found in the mud and electrolyte, the amount deposited with the copper being extremely small when the refinery is running under proper conditions. A certain amount may get on the cathode mechanically, either by having the anode too close or by unnecessarily stirring up the mud.

45. Lead is attacked by the electrolyte before the copper and passes into the slimes as lead sulphate. It has no tendency to deposit on the cathode. Its only injurious effect is to make the electrolyte poorer in copper and acid.

46. Bismuth and **bismuth oxide** are dissolved and pass for the most part into the slimes in the form of basic sulphate.

47. Arsenic dissolves in either acid or neutral solutions and passes into the electrolyte until the latter becomes saturated with it; from that time on it passes into the slimes. Arsenic trioxide combines in neutral solutions with cuprous oxide or other metallic oxides and passes entirely into the slimes, as these arsenites are non-conductors of electricity. In an acid bath the arsenic slowly dissolves and passes into the solution as arsenic acid H_3AsO_4. Arsenic in the anodes makes the electrolyte richer in acid, but poorer in copper. The copper deposited from neutral solutions will contain arsenic, but that from acid solutions will be free from the impurity unless the bath contains proportionately little copper or is run at a high current density.

48. Antimony is partly dissolved in acid or neutral solutions and partly remains at the anode as a basic sulphate, while a part of that dissolved separates again as basic sulphate after having stood for some time. Antimoniates in the anode, being non-conductors, pass into the slimes, where they are slowly dissolved in acid solutions with a separation

of antimonic acid H_3SbO_4; the bases that are combined with it tend to neutralize the solution.

As long as the solution is acid and contains the proper amount of copper and acid, no antimony will be deposited with the copper, but some basic salt may be held mechanically, making a black, muddy deposit. If, however, the solution should become nearly or quite neutral, antimony will be deposited with the copper, making it dun colored and brittle, and it will often be characterized by long, needle-like excrescences bounded by rectilineal planes. Also, if the electrolyte is too poor in copper, no matter if the correct proportion of acid is present, antimony will be deposited with the copper. *High current density has the same effect as an impoverishment of copper.*

49. Selenium and tellurium are probably present in anode copper as selenide and telluride of silver or copper. They have but very little effect upon the purity of the copper deposited.

50. Oxygen is present principally as cuprous oxide and also combined with some of the other impurities. It sends copper into the slimes, but that is afterwards dissolved in the excess of acid, causing the solution to get stronger in copper sulphate and weaker in acid.

51. Tin is dissolved, but is precipitated some time afterwards as a basic sulphate. Tin is considered rather a beneficial than an injurious impurity of cathode copper.

The presence of tin causes the bath to become weaker in copper, but only a small proportion of tin is taken up by the solution. The effect is to cause the solution to become slightly more acid.

The presence of tin in the electrolyte has, moreover, a marked beneficial influence on the quality of the deposited copper; for while a bath containing a chemically pure neutral solution of copper sulphate with a current of 1.8 amperes per square foot gives a warty and brittle deposit, the same current gives a smooth, malleable copper when the anodes contain a sufficient amount of tin. The tin is not, however,

deposited with the copper, but probably combines with the arsenic, if present, carrying it into the slimes.

52. Gold goes entirely into the slimes and so has no injurious effect on the deposited copper.

53. Silver goes into the slimes, but if the solution is neutral it may be dissolved and deposited at the cathode. Cathode copper may often contain small quantities of silver, but it is thought to be deposited mechanically from suspended residues rather than electrolytically. It is advisable, however, to have a slight trace of hydrochloric acid present in the electrolyte to precipitate any silver that may get into solution.

54. Iron, nickel, cobalt, and zinc are dissolved more readily under the action of the electric current than copper, and hence their effect is to weaken the solution with respect to copper and free acid and to load it with salts.

Iron dissolves, forming ferrous sulphate, which is oxidized by air to ferric sulphate. If the copper in the electrolyte is so far replaced by iron that the solution contains but 2 grams of copper per liter, the deposit at the cathode becomes warty or sprouted. Iron is not deposited in acid solution, but its presence may affect the polarity of the other elements. For instance, if ferric iron is present, some silver will go into the solution and be deposited. If ferrous iron is present, there is a greater tendency for bismuth, antimony, and arsenic to go into the solution and be eventually deposited.

55. Copper Sulphate in Electrolyte.—In order to keep the solution in good condition, it is necessary to add sulphuric acid from time to time to make up for the losses, also copper sulphate, if needed. The solution becomes more and more impure; this has a bad effect upon the deposited copper and at the same time it may increase the resistance of the bath.

Copper sulphate is formed in the electrolyte more rapidly than copper is deposited, owing to the ordinary chemical reaction of the copper and copper oxide in the excess of acid,

so that after some time there is an accumulation of it that must be removed.

In an acid solution the cuprous oxide is decomposed by a secondary reaction, probably forming cuprous sulphate, which is oxidized by the air to cupric sulphate. This oxidation to the cupric form seems necessary to the production of a pure and crystalline deposit of copper, hence the necessity of a good circulation of the electrolyte to bring it in contact with the air.

56. Purifying the Electrolyte.—There are two distinct methods used for removing impurities from the electrolyte. One is the partial removal of the impurities, such as bismuth, arsenic, antimony, iron, etc., from the solution. This removal, which has not, however, given general satisfaction, may be accomplished by precipitating the antimony, arsenic, bismuth, and iron by means of copper oxide or lime; by boiling with metasstannic acid to precipitate arsenic; or by the oxidation of impurities by means of air forced into the solution. The last method is based upon the belief that the impurities, arsenic, antimony, silver, etc., are deposited mechanically rather than electrolytically, and the object is to get the suspended impurities into solution by oxidation with jets of air.

Air under 3 or 4 pounds pressure is therefore forced into a pipe at the bottom of the tank in such a way that the solution is forced up through a pipe and is delivered into the upper part of the tank through a large number of small perforations in the pipe. In this way a thorough circulation of the electrolyte is maintained and at the same time the solution is thoroughly oxidized by the air jets.

Although this treatment has not the importance at first attached to it, especially in the removal of the arsenic, it is very beneficial if assisted by the general circulation of the solution.

57. Where anodes contain considerable arsenic, alloying them with tin is beneficial, for the arsenic combines with the

tin to form an insoluble compound, both elements then going into the slimes. With smaller quantities of arsenic, although the effect is good, it does not pay.

58. Another method for purifying the electrolyte is to draw off part of the solution and add fresh in its place, the valuable materials in the portion removed being recovered by one of several methods. This process is generally considered the more satisfactory, and is the one used in many of the larger refineries.

It is not necessary for the solution to be kept absolutely pure, but the percentage of impurities should be kept within certain limits. This is accomplished by removing from the system at regular intervals a portion, say one-fifth of the electrolyte, and replacing it by fresh solution. By doing this at such intervals that the impurities can never rise above a certain percentage, the solution in the tanks is kept in a healthy working condition.

59. The discarded portion of the solution is valuable for the copper it contains and also for some of the impurities, as arsenic, nickel, etc. Several methods are used for recovering these substances. The copper is often recovered as copper sulphate in the following way: The solution is boiled in lead-lined tanks with scrap copper in the presence of steam and air. By this treatment the free sulphuric acid is converted into sulphate of copper and the copper contents thereby increased. When this is completed the solution is pumped into the crystallizing tanks, where the copper sulphate crystallizes out. This copper sulphate is now sufficiently pure to be used in making up new solution or to be put upon the market as blue vitriol.

The mother liquid remaining after the copper sulphate has crystallized still contains considerable copper, together with practically all the arsenic, antimony, bismuth, iron, etc. This may be evaporated down and all the remaining copper sulphate allowed to crystallize out, together with the arsenic. Their separation depends on their difference in solubility.

The mixed crystals are next leached with just sufficient water to dissolve the copper sulphate, leaving the arsenic acid unaffected. The arsenic acid can be used for making various arsenic compounds, as Scheele's or Paris green. The residual mother liquor can be further worked for sulphuric acid or sulphate of iron (green vitriol or copperas).

In some refineries this first mother liquor, which was obtained from the first crystallization of copper sulphate, is treated with scrap iron, upon which the copper is precipitated and then the arsenic. This precipitate is either worked up into base copper or is used in the manufacture of compounds of arsenic.

60. A very satisfactory method for the purification of electrolytes is to precipitate the copper and arsenic in special tanks, using insoluble lead anodes, the strength of current being such that all the impurities but the iron are precipitated with the copper. The deposit may be afterwards worked up for copper by well-known methods.

The solution, now freed from the most harmful impurities, is restandardized and used over. When the proportion of iron becomes too great, however, it must be discarded and the copper recovered as blue vitriol by crystallization or it must be precipitated on metallic iron.

61. Copper Sulphate Tanks.—A crystallizing plant is considered a necessary, although expensive, adjunct to a refinery, even if other processes are used.

The particular process to be used at a refinery will depend largely on local conditions. For instance, it would not pay to turn out bluestone for the market if the works were situated a long way from those markets. Again, if power was dear, it might not pay to deposit the copper from the copper sulphate by using insoluble anodes.

62. Cleaning Out Tanks.—At regular periods, usually every 2 or 3 weeks, the cathodes are removed and the tanks cleaned out. The slimes containing the impurities are not necessarily cleaned out as often, but that will depend on the

quantity of slimes and the amount of gold and silver contained in them. If the quantity of slimes is abundant, it forms a more or less conducting layer on the bottom of the tank, and if sufficient is present to reach the bottom of the electrodes, a short circuit will result. Should the value of the gold and silver in the slimes be large, it is not desirable to allow the amount of money they represent to lie idle longer than is necessary. The slimes are usually removed at intervals of from 2 to 4 weeks, but they are not worked up until sufficient have accumulated to make it worth while to start the separating plant.

63. When it is desired to clean out the tanks, a complete row is taken of, say, 10 tanks and the solution flowing in from the storage vats to the highest tank is shut off. These tanks are next cut out of electrical circuit. The means for doing this will depend on the arrangement of the conductors, but it is frequently done by clamping a copper bar across the conductors on opposite sides of the tank, so that the current will pass through the bar instead of between the electrodes. The solution is now siphoned into a launder running along the side of the tanks and which communicates with the lower storage vat. Sometimes the solution is siphoned directly into the lower storage vat by means of a rubber hose or into the upper storage tank by means of a portable steam ejector. Care should be taken not to disturb the slimes in the bottom of the tank, and the solution should not be siphoned off closer than within 6 inches of the bottom.

64. Removing Cathodes and Slimes.—After the cathodes have drained they are removed from the tanks and placed on a 4-wheeled truck running on tracks in the passageway between each two double rows of tanks. They are next washed and then melted down and cast into wire bars or ingots or else sold as they are. The anodes are now pushed up

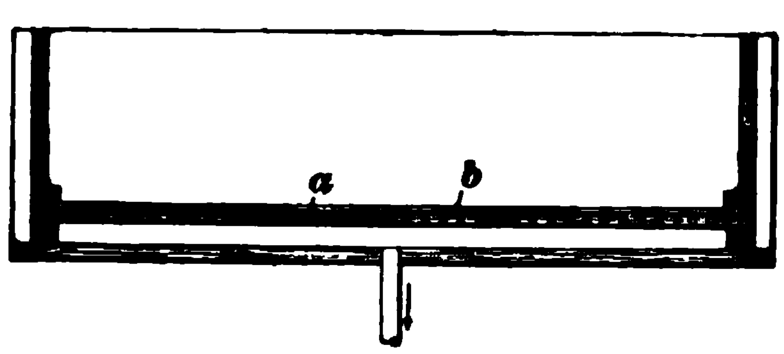


FIG. 15

to one end of the tank and the slimes shoveled into a barrel standing on a 4-wheeled truck. When the greater part has been taken out, the anodes are washed and scraped and the slimes from these removed, the anodes themselves being sent to the scrap heap to be remelted. A rubber hose is now connected to the lead pipe, fastened into the bottom of the barrel containing the first lot of slimes, and the slimes are run on to a 16-mesh screen, upon which the copper scrap, often amounting to a considerable quantity, is caught and sent back to the anode furnace. When the slimes have settled, the solution is drawn off the top and sent back to the refinery. The second lot of slimes, which has been washed off the anodes, is then added to the first and the two mixed together with the addition of more water, if necessary. They are then run into a tank such as is shown in Fig. 15, with a perforated false bottom *a*, upon which flannel *b* is stretched. The solution that runs through this filter is used to make up fresh electrolyte. Any further washings from the slimes are usually thrown away.

TREATMENT OF TANK RESIDUES

65. The residues in the bottom of the tanks contain practically all the silver and all the gold, together with *Pb*, *Bi*, *As*, *Te*, *Se*, *Zn*, and some copper compounds and fragments of copper scraps from the disintegrated anodes. Residues are either treated at the works or sold to silver refiners. At present the residues are worked for their gold, silver, and copper, all other elements being allowed to go to waste.

66. Thofehrn's process for the treatment of copper-refinery slimes consists in allowing them to lie exposed to the atmosphere for a certain length of time and then melting them down in order to free them from base metallic oxides. This is done in a small refinery furnace lined with magnesia brick, which are not corroded by the slags. The fusion produces a copper matte containing all the silver and gold. This matte is cast into plates, which are submitted

to electrolysis in special tanks, and the copper recovered pure enough to put upon the market. The residues from this treatment contain silver enough to be treated by the concentrated sulphuric-acid H_2SO_4 process.

67. Cabell-Whitehead Process.—In this process the slimes are treated with silver sulphate $AgSO_4$ and sulphuric acid, the copper in the slime is dissolved, and one equivalent quantity of silver deposited. The silver thus obtained free from copper is washed to remove copper sulphate and melted into bars. This process is used at the works of the Baltimore Smelting and Refining Company.

68. Direct Treatment With Concentrated Sulphuric Acid H_2SO_4.—Although this method is not much used now, a short description of it will be of interest. The residues are dried and sifted to remove scrap copper, as previously described; they are then treated directly or after melting them with hot concentrated H_2SO_4. This dissolves any copper or silver in them, the gold remaining as a residue unaffected. The silver in the solution is precipitated on copper plates, the copper sulphate formed being saved by crystallization.

69. Direct Treatment With Sulphuric Acid H_2SO_4 **and Air.**—This is really a modification of the previous method. The screened residues are placed in a lead-lined tank, in the bottom of which is a perforated lead pipe connected with a steam pipe and a Körting injector, having a short inner tube and an air opening. To the same residue is added the proper amount of sulphuric acid; steam and air are then forced through the mixture. On account of the condensation of the steam, concentrated H_2SO_4 is added at first, but in smaller quantity than in the previously described processes. The hot acid rapidly dissolves any copper present, liberating at the same time sulphur dioxide SO_2, which reacts upon the copper sulphate present, reducing it to cuprous sulphate and at the same time forming sulphur trioxide SO_3, which unites with water H_2O and forms sulphuric

acid H_2SO_4. The oxygen of the air immediately reoxidizes the cuprous sulphate to cupric sulphate. Thus the residues are freed from copper and are proportionately richer in silver and gold.

These residues are filtered and washed to free them from any traces of copper, the liquor and wash water being used in the preparation of new electrolyte or otherwise worked for its copper contents. The rich slimes, now free from copper, are dried and melted down at a low red heat to a base bullion. The arsenic and antimony are volatilized in an oxidizing flame and the gold and silver are now ready for parting.

This process is used at the Anaconda works and gives satisfaction.

70. Efficiency of a Refinery and How to Maintain It.—The efficiency of a refinery is dependent on many small details that can only be kept in check by proper attention on the part of the superintendent. A voltmeter should be constantly used, as anything unusual with the voltage is a sure indication that there is something wrong. In large refineries, it is customary to keep one man exclusively employed going from tank to tank with a voltmeter whose terminals are connected to two spikes on a strip of wood. This strip is laid across the vat so that a spike touches each conductor and the reading taken on the voltmeter. Since the voltmeter is carried in the hand and at the time the reading is taken it is frequently out of the vertical, an instrument having a spring and not a gravity control should be used.

An electric bell has been used for the same purpose with good effect. The bell is wound with wire of such a resistance that it will ring with about its normal loudness when the tank is working at its correct voltage. Should the voltage rise or fall, the bell will ring louder or softer as the case may be. With a little practice, a man can tell just as accurately with this as with the best voltmeter; it is a good deal cheaper and is quicker to use.

71. Voltmeters.—At some works a wire is run from every tank into the manager's office, where a switchboard is arranged in such a way that the voltage of any tank can be taken at a moment's notice. This is somewhat expensive to install, but it saves so much labor that it will more than pay for itself. If the voltmeter reading is *higher* than usual, it indicates that there are probably dirty contacts somewhere; or that there is a thick layer of mud, which is more or less non-conducting, on the surface of the anode; or that the solution is getting weaker in free acid and is consequently of greater resistance; or that some polarization is taking place owing to inferior circulation of the solution.

72. If the voltmeter reading is *lower* than usual, it indicates that there is short-circuiting either by the electrodes not hanging parallel, or more probably by the copper "sprouting," particularly at the edges of the cathode and so coming into contact with the anode. If this happens, there is usually a dead short circuit and the voltmeter refuses to give any deflection at all. When this takes place it is a pretty sure sign that the cathodes want changing, but may be temporarily remedied by altering the position of the offending cathode a little and giving it more space by moving the other plates a little closer together. If a thin strip of wood is passed between the electrodes, one may be lucky enough sometimes to knock off the nodule of copper that is doing the mischief.

Another cause for the low reading of the voltmeter is short-circuiting through the mud, that is to say, the layer of mud on the bottom of the tank has got so deep that it is touching the bottom of the electrodes. There is only one remedy for this, and that is to clean out the tank and remove the mud.

73. Chemical Reactions in Tanks.—It is a good plan for the purpose of seeing whether the efficiency is well maintained to weigh the cathodes from one of the tanks, then by keeping careful note of the length of time they have been depositing and the average current during that period,

the efficiency can be calculated by dividing the amount actually deposited by the amount that theoretically should have been deposited. The efficiency is given in percentage if the result is multiplied by 100.

Another cause for loss of efficiency is the presence of iron salts. In the presence of sulphuric acid, ferrous salts are oxidized to ferric at the anode, thus

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$$

The ferric salt then getting to the cathode is reduced back to the ferrous state, thus

$$Fe_2(SO_4)_3 + H_2 = 2FeSO_4 + H_2SO_4$$

Part of the current that should be doing useful work in dissolving and depositing copper is occupied in oxidizing and reducing iron salts. If these are present in appreciable quantities, there will be a corresponding lowering of efficiency.

74. Physical Tests for Refined Copper.—By far the largest portion of electrolytic copper is used for electrical conductors; it is therefore important to put it under such tests as will best determine its suitability for this purpose. From every furnace charge of, say, 12 tons, two or three test bars are taken during casting, each bar weighing 6 to 12 ounces each. These are then stamped with the date and number of the furnace, etc. and sent to another department, where a wire $\frac{1}{16}$ inch diameter and about 20 feet long is drawn from one or all of the bars. This wire, together with the rest of the bar, is sent off to the physical testing laboratory, where it is tested for its electrical conductivity, tensile strength, elongation, and twisting or torsional limit.

75. Electrical Conductivity.—The diameter of the wire is ascertained by carefully measuring the diameter in four or five places by means of a micrometer or self-registering caliper and taking the average of these readings. The resistance of the wire is tested by means of a Wheatstone bridge or a delicate ohmmeter, and after noting the temperature of the room the results are compared with a table of

standard results and from these the conductivity is calculated.

Reference may here be made to what at first may appear rather confusing. Wire is frequently quoted as over 100 per cent. conductivity. Years ago a celebrated chemist named Matthiessen, with a view of getting a standard of conductivity for copper, prepared by chemical means what he considered to be absolutely pure copper. The results of his tests were generally accepted, but it afterwards turned out that the copper he had prepared was not absolutely pure and he had consequently obtained too low a standard, but his results had become so firmly established that it was not thought advisable to alter them. Hence copper is often seen quoted as 102 per cent. Matthiessen standard. It is interesting to note that it is now possible to produce commercially, by electrolytic means, purer copper than it was possible to prepare chemically when every conceivable precaution was used. Absolutely pure copper is 102.38 per cent., Matthiessen's standard.

76. Tensile Strength and Elongation.—About 2 feet of the wire to be tested is cut off and placed between the grip clutches of a Riehle machine and its tensile strength ascertained. The pull on the wire is increased gradually until it breaks. The tensile strength calculated from the rupture of the wire is usually given in pounds per square inch.

The elongation is determined from the same sample by placing the two broken ends together and measuring the increase in length of the wire.

77. Twisting Limit.—Half a dozen pieces of wire, each about 4 inches long, are cut off and placed in a simple twisting machine, and the number of complete twists each will stand is noted and the average of the six taken.

The results from all these tests are carefully recorded in a book, and should any of them not come up to the required standard, another bar is tested. Should results be still unsatisfactory, a sample is sent to the chemical laboratory for

further investigation. When the trouble is discovered, the superintendent or those responsible are notified so that they may remedy it, and the particular wire bars belonging to that charge are rejected.

78. Account Books.—It is usual to keep account books showing the product account, that is to say, all that goes into the refinery and all that comes out. The two should, of course, balance; if they do not, it is a sure sign that there is waste going on somewhere and the matter should be investigated.

The anodes are carefully weighed and sampled and their total contents of valuable products, i. e., copper, gold, and silver, carefully calculated from the results of the chemical analysis. Any bluestone sent into the refinery is also weighed, sampled, and analyzed. The sulphuric acid is not usually reckoned in the product account.

In the same way, everything that comes out of the refinery, such as refined copper, slimes, electrolyte, scrap anode, etc., is weighed, sampled, and analyzed for copper, gold, and silver and the total contents in tons of copper or ounces of gold and silver carefully calculated. All that goes in is entered on the debit side and all that comes out is entered on the credit side, and if everything is going well the two sides should balance.

CHEMICAL ANALYSES REQUIRED IN COPPER REFINERIES

79. Chemical Tests.—The chemical analyses necessary in a refinery play a most important part, the penalty for their neglect being the production of impure copper and losses of gold and silver. Besides this, they are necessary for the purpose of keeping the product account books in proper order. In Table V the frequency of taking analyses for various materials in a large refinery in the United States is shown.

TABLE V

Frequency of Determination	Material	Determinations
Daily	Solutions (electrolyte)	Sp. Gr. $CuSO_4$ and free H_2SO_4
	Copper bullion and anodes	*Cu*, *Ag*, *Au*
Weekly	Cathodes	*Cu*, *Ag*, *As*, *Sb*
	Slimes	*Cu*, *Ag*, *Au*
	Silver slabs	*Ag*, *Au*
	Gold bar	*Au*
	Solutions	*As*, *Sb*, *Fe*, *Cl*
Occasional	Blister and refinery slags	*Cu*, *Au*, *Ag*
	Cement copper	*Cu*, *Ag*, *As*
	Wire bars	*Cu*, *Ag*, *As*, *Sb*
	Pig copper	*As*
	Blast-furnace slags	*Cu*
	Blast-furnace pots	*Cu*, *Ag*, *Au*
	Coal, limestone, boiler scale, water, ore, matte, etc	various

ANALYSIS OF ELECTROLYTE

80. Determination of Free Sulphuric Acid.—Take 5 cubic centimeters (c. c.) of the electrolyte in a beaker of about 250 or 300 c. c. capacity. From a burette add an excess of a normal solution of caustic soda $NaOH$. For an indicator use a weak alcoholic solution of phenolphthalein. This is red in alkaline solutions and colorless in acid. Then 1 c. c. = .04 gram $NaOH$ will neutralize .049 gram H_2SO_4.

$$2NaOH + H_2SO_4 = Na_2SO_4 + H_2O$$

Since 1 atom of sodium displaces 1 atom of hydrogen,

$$80 : 98 = .04 : .049.$$

Boil until the copper is all precipitated as the black oxide. Filter through an asbestos filter, using the filter pump if necessary, and wash the oxide thoroughly with hot water. Now titrate the excess of $NaOH$ in the filtrate, to which the wash water has been added, with a standard solution of

sulphuric acid, 1 c. c. of which contains .049 gram of H_2SO_4. One cubic centimeter will be equivalent to 1 c. c. of the standard caustic-soda solution. The number of c. c.'s required subtracted from the number of c. c.'s of $NaOH$ solution used gives the number of c. c. of $NaOH$ solution neutralized.

After determining the weight of copper in the precipitated oxide by the method described in the next article, calculate how much of the soda solution was neutralized by the sulphuric acid in combination with the copper. One gram of copper neutralizes 1.555 grams of H_2SO_4 in forming $CuSO_4$. Multiply the weight of Cu found by this and divide the result by the H_2SO_4 value of 1 c. c. of the caustic-soda solution; this gives the number of c. c.'s of the latter neutralized by the H_2SO_4 combined with the copper. The difference between the total volume of soda solution neutralized and the volume neutralized by the combined acid will give the volume neutralized by the free acid. This volume multiplied by .049 gram gives the weight of free H_2SO_4 in 5 c. c. of electrolyte.

81. Determination of the Copper.—Dissolve the carefully washed copper oxide, obtained as described, in strong nitric acid, using only enough acid to completely dissolve it. Add ammonia water until the precipitate formed on the first addition dissolves to a blue solution and titrate with the standard potassium-cyanide solution, as described in *Assaying*.

82. Example.—Take 5 c. c. of the electrolyte and add 35 c. c. of normal caustic-soda $NaOH$ solution. The back titration for excess of soda solution requires 5 c. c. of standard sulphuric-acid H_2SO_4 solution of the strength given. 35 c. c. − 5 c. c. = 30 c. c. of soda solution neutralized by the electrolyte. The copper found in the oxide is equal to .2 gram.

Now, 1 gram of copper neutralizes 1.555 grams of H_2SO_4, so the .2 gram will neutralize .311 gram of H_2SO_4, which is equivalent to 6.34 c. c. of soda solution. Or, more directly,

the weight of the copper times 31.70 gives the number of c. c.'s of soda solution neutralized (5 c. c. × 6.34 c. c. × .2 gram = 31.70). Or, 30 c. c. − 6.34 c. c. = 23.66 c. c. of soda solution neutralized by the free sulphuric acid. 23.66 c. c. × .049 = .934 gram H_2SO_4 in 5 c. c. of electrolyte. The per cent. by weight is determined by dividing the weight in 100 c. c. by the specific gravity of the solution.

83. Arsenic in the electrolyte is usually determined by the distillation method, as follows: Introduce into a small retort or distilling bulb 10 c. c. of electrolyte, add a crystal of ferrous sulphate $FeSO_4$ and 20 c. c. of concentrated hydrochloric acid HCl and distill nearly to dryness. The arsenic distills over as arsenic trichloride $AsCl_3$. Collect the distillate in a beaker containing about 50 c. c. of distilled water. Let the end of the tube dip beneath the surface of the water to prevent loss.

Great care must be taken to heat the bulb steadily and to remove the beaker at the end of the operation before removing the flame from the bulb. If this precaution is not taken some of the water will be drawn into the bulb and cause an explosion.

Neutralize the solution with caustic soda and then add 20 c. c. of a saturated solution of sodium carbonate Na_2CO_3 and 10 c. c. of starch solution and titrate with standard iodine solution till starch turns blue. The reaction that takes place is expressed by the equation

$$Na_3AsO_3 + I_2 + H_2O = Na_3AsO_4 + 2HI$$

84. Preparation of Standard Solution of Iodine.—Weigh out carefully 2.558 grams of resublimed iodine into a 1-liter measuring flask. Dissolve 3 grams of pure potassium iodide in 100 c. c. of distilled water, add to the iodine in the measuring flask and gently shake until the iodine is dissolved. Dilute to 1 liter with distilled water at 15° C.

This solution will be of such a strength that 1 c. c. will indicate .001 gram of arsenic trioxide As_2O_3. It should be kept in a dark-colored bottle in a dark place and should be

checked frequently against a solution containing a weighed amount of As_2O_3, made by dissolving the As_2O_3 in hydrochloric acid HCl; distilling with ferrous sulphate $FeSO_4$, neutralizing with sodium hydrate $NaOH$, and sodium carbonate Na_2CO_3 added as in the regular assay.

85. Antimony in the Electrolyte.—Take 20 c. c. of the solution and add ammonium hydroxide NH_4OH until alkaline and pass in hydrogen sulphide H_2S until saturated, or add ammonium sulphide $(NH_4)_2S$. Boil to settle the precipitate and filter hot; then wash precipitates thoroughly with hot water containing a little $(NH_4)_2S$. The antimony sulphide formed will be dissolved by the $(NH_4)_2S$ and so go into the filtrate. From the alkaline-sulphide solution precipitate the antimony and arsenic sulphide by adding hydrochloric acid HCl. Filter, wash the precipitates with hot water, and dissolve out the antimony sulphide in a little warm concentrated HCl. The sulphide of arsenic will remain undissolved. Filter and wash again, dilute the filtrate, and reprecipitate the antimony with H_2S. Let settle, filter, and transfer the residue to a porcelain crucible, ignite and weigh as antimony tetroxide Sb_2O_4.

86. Iron in the Electrolyte.—Take 100 c. c. of the electrolyte and add a few drops of strong nitric acid HNO_3 to oxidize any ferrous sulphate to ferric sulphate, then add an excess of ammonium hydroxide NH_4OH, and boil a few minutes to settle the precipitate. Filter, wash, and redissolve the precipitate in a slight excess of hydrochloric acid HCl. Dilute, pass in hydrogen sulphide H_2S, and filter. Boil the filtrate to expel all traces of H_2S and add an excess of NH_4OH, filter, and wash the precipitated ferric hydroxide $Fe(OH)_3$ with hot water. Dissolve in dilute sulphuric acid H_2SO_4, reduce with zinc, and proceed as described in *Assaying*.

87. Chlorine in the Electrolyte.—Take 100 c. c. of electrolyte, dilute, heat, and precipitate the chlorine as

silver chloride $AgCl$ with a little silver nitrate $AgNO_3$. Filter and wash the precipitate thoroughly with hot water. Scorify the filter paper and the precipitate with a little test lead and cupel. The weight of the silver button times .32855 gives the weight of chlorine Cl.

A quicker method is to filter the silver chloride upon a weighed Gooch crucible. Dry the precipitate in an air bath at 100° C and weigh again. The increased weight of the crucible is the weight of $AgCl$. This weight times .2473 gives the weight of Cl.

ANALYSES OF ANODE AND CATHODE COPPER

88. Sampling.—Anode plates and cathodes are sampled for chemical analysis by boring into them in various places with a machine drill and mixing the borings thoroughly to obtain an average sample. Melting and granulation of the borings is not advisable, as more or less oxidation takes place, so that the results of analyses are not accurate.

89. Copper Determination.—Take 1 gram of anode drillings and dissolve in nitric acid HNO_3. If the sample is not uniform, 20 grams may be taken and one-twentieth of the resulting solution used. Dilute and add 1 or 2 drops of dilute hydrochloric acid HCl to precipitate silver. Filter into a weighed platinum dish or beaker and electrolyze. Although the copper may be deposited from a nitric-acid solution, it is better to use a sulphate solution containing a very little HNO_3. To get this, add a slight excess of sulphuric acid H_2SO_4 to the nitrate solution before diluting and warm on the sand bath until white fumes of H_2SO_4 begin to come off. Now dilute, add a few drops of HNO_3, and proceed with the electrolysis. The HNO_3 prevents deposition of arsenic and antimony with the copper.

90. For an anode a spiral of heavy platinum wire is used; for a cathode a piece of platinum foil, a platinum

crucible, or a platinum dish. Fig. 16 shows the beaker, spiral anode, and curved cathode used for the test. The beaker holds the electrolyte and the electrodes. The projecting wires on the electrodes connect with a battery. The cathode upon which the copper is deposited should not be entirely submerged, but should project from $\frac{1}{4}$ to $\frac{1}{8}$ inch above the surface of the liquid. Two cells of a crowfoot battery give sufficient current.

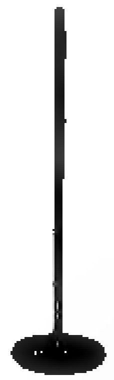


FIG. 16

To economize time, the assays should be prepared so that the deposition can go on during the night and be complete by the next morning. To test when the deposition is complete, lower the cathode a little deeper into the solution. If the copper is all deposited, the clean platinum surface, which was previously above the solution, will remain white, but if there is still copper in the solution, it will be deposited on the bright platinum so that it will show copper coloration. In this latter case the deposition must be continued until all the copper is down.

As soon as the deposition is complete disconnect the wires, remove the cathode immediately, and wash the deposit thoroughly, first with hot water and then with wood alcohol. Let it cool in a desiccator and weigh. This weight, less the original weight of the cathode, gives the quantity of copper deposited.

91. Arsenic in Refined Copper.—Dissolve from 20 to 30 grams of drillings in nitric acid HNO_3 and heat to expel brown nitrous fumes; then add about 1 gram of crystallized ferric sulphate $Fe_2(SO_4)_3$; stir and add an excess of ammonium hydroxide NH_4OH; heat to boiling, and filter off the ferric hydroxide $Fe(OH)_3$, which contains all the arsenic. Wash with hot water, dry, and fuse in a porcelain crucible with 7 or 8 parts of a mixture of potassium nitrate KNO_3

and sodium carbonate Na_2CO_3. When fusion is complete, dissolve with hot water and filter. The arsenic is now all in solution in the filtrate as sodium or potassium arsenate. Add carefully HNO_3 until slightly acid and boil to expel carbon dioxide CO_2 and brown fumes. Now, add just sufficient NH_4OH to make the solution very slightly alkaline. If any precipitate forms, filter. A slight excess of a neutral solution of silver nitrate $AgNO_3$ is now added. Stir and test with litmus, and if acid, neutralize again with NH_4OH. The arsenic will be precipitated as the arsenate of silver Ag_3ASO_4, which is of a brick-red color. Filter and wash the precipitate with hot water. Care must be taken not to allow the solution to become acid. The silver in the precipitate is now determined by scorifying with test lead and cupeling the button. Or, volumetrically, by dissolving in dilute HNO_3 on the filter and titrating the silver by means of a standard solution of ammonium sulphocyanate NH_4SCN containing about 5 grams of the salt to the liter. Use for an indicator 5 c. c. of a saturated solution of ferric ammonium sulphate $Fe(NH_4)(SO_4)_2 + 12\,H_2O$. Any excess of sulphocyanate solution above that required to precipitate the silver gives a permanent red coloration. The weight of the silver found times .23148 gives the weight of the arsenic.

92. Antimony and Bismuth in Copper.—Dissolve from 10 to 30 grams of copper drillings in nitric acid HNO_3, heat to drive off the brown fumes, dilute to 300 c. c., and add a small crystal of pure ferric sulphate $Fe_2(SO_4)_3$ to convert the arsenic and soluble antimony into iron salts.

Add an excess of ammonium hydroxide NH_4OH, boil, and add .75 gram of ammonium carbonate $(NH_4)_2CO_3$ and a little sodium phosphate Na_2HPO_4; these will completely precipitate the antimony and bismuth. Filter and wash the precipitate with water containing a little ammonium hydrate NH_4OH. Dissolve the precipitate in dilute hydrochloric acid HCl, dilute to about 75 or 100 c. c. and pass in hydrogen sulphide H_2S for 30 minutes. Now add 10 c. c. of

yellow ammonium sulphide $(NH_4)_2S_2$ and warm gently for 1 hour to dissolve the sulphides of antimony and arsenic. Filter, wash, and precipitate the antimony trisulphide Sb_2S_3 and arsenic trisulphide As_2S_3 in the filtrate by adding dilute HCl. Filter, wash, and dissolve the Sb_2S_3 by warming with a little concentrated HCl. The As_2S_3 will remain undissolved. Filter and dilute the filtrate, pass in H_2S to reprecipitate the antimony as sulphide. Wash by decantation and transfer to a weighed porcelain crucible. Ignite and weigh the antimony as antimony tetroxide Sb_2O_4.

The residue from the ammonium-sulphide treatment contains all the bismuth, possibly some lead and copper. Dissolve in HNO_3 and precipitate the bismuth with NH_4OH and ammonium carbonate $(NH_4)_2CO_3$. Filter and wash the precipitate with water containing a little ammonia. If not free from copper, dissolve in HNO_3 and reprecipitate. Dissolve the precipitate in HNO_3 and determine bismuth electrolytically in a dilute solution. The operation is conducted in the same manner as for copper.

Or, dry the precipitate and filter paper, remove the former as completely as possible to a weighed porcelain crucible; burn the filter and add the ash to the precipitate; ignite and weigh as bismuth trioxide Bi_2O_3.

93. Lead and Iron in Copper.—Dissolve 10 to 30 grams of the borings in a beaker of about 300 c. c. capacity, with nitric acid (1 part strong HNO_3 to 1 part H_2O). Use as little acid as possible. When the copper is all in solution, heat to drive off the excess of acid. Dilute to about 300 c. c. and add 1 c. c. of sulphuric acid H_2SO_4, stir thoroughly, and let the solution stand several hours to allow the lead sulphate $PbSO_4$ to settle. Filter and wash the precipitate thoroughly with a 1-per-cent. solution of H_2SO_4. Dissolve the $PbSO_4$ on the filter with a warm and slightly acid solution of ammonium acetate; then dilute to 250 c. c. and titrate the lead with a standard solution of ammonium molybdate $(NH_4)_2MoO_4$, containing 9 grams of the salt to the liter. One cubic centimeter of this solution is equivalent

to .01 gram of lead. The solution should be standardized against weighed quantities of pure $PbSO_4$ dissolved in ammonium acetate and diluted as for the regular assay.

For an indicator, a weak solution of tannin is used, 1 gram of tannin to 300 c. c. of water. This is used on a spot plate. As soon as an excess of molybdate solution has been added to the lead solution, a drop of the latter touched to a drop of the tannin solution on the spot plate will give a yellow coloration.

To the filtrate from the lead sulphate add ammonia in excess and boil. The iron, arsenic, etc., will be precipitated. Filter and wash the precipitate thoroughly with hot water to remove copper. Dissolve the precipitate on the filter with a little hot dilute hydrochloric acid HCl, dilute and pass in hydrogen sulphide H_2S for ½ hour. Filter and wash the precipitate with H_2S water. Boil to remove all traces of H_2S, acidify strongly with H_2SO_4 and reduce with zinc, as described in *Assaying*, and titrate with a standard solution of potassium permanganate.

94. Selenium and Tellurium.—Dissolve 25 to 50 grams of the copper borings in nitric acid HNO_3, heat to drive off brown fumes, and add 1 gram of ferric nitrate, stir and boil. Add an excess of ammonium hydroxide NH_4OH. The precipitate will contain iron, arsenic, selenium, tellurium, etc. Filter, wash the precipitate with water containing a little NH_4OH, and dissolve in a little warm dilute hydrochloric acid.

To the solution add 1 gram of tartaric acid $C_4H_4O_4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$ make alkaline with potassium hydrate KOH, and pass in hydrogen sulphide H_2S for ½ hour. Filter and add an excess of hydrochloric acid to the filtrate to precipitate the sulphides of selenium, tellurium, etc. Warm to expel H_2S and filter off the sulphides of selenium and tellurium, etc. Wash and dissolve the precipitates in aqua regia, evaporate to dryness to expel the nitric acid, twice if necessary, and dissolve in hydrochloric acid. Precipitate the selenium and

tellurium by passing sulphur dioxide SO_2 into the solution. Filter upon a weighed filter, wash with warm water, let stand in a warm place to dry for 12 hours, and weigh.

To separate the selenium and tellurium, place the precipitate in a small casserole, add an excess of a strong solution of potassium cyanide, and boil. As soon as the precipitate is dissolved, add hydrochloric acid. This will precipitate the selenium, but not the tellurium. Filter, wash, dry at 100° C., and weigh the selenium. The tellurium is found by difference.

95. Sulphur.—Dissolve 10 to 20 grams of copper in 60 c. c. of nitric acid (1.42 specific gravity) and 15 c. c. of hydrochloric acid (1.2 specific gravity). Heat over an alcohol flame (gas contains sulphur, which may interfere with the accuracy of the analysis) until dissolved, then raise the heat and evaporate nearly to dryness. Add 50 c. c. of strong nitric acid HNO_3 and evaporate again. Repeat again and dissolve in 300 c. c. of water; add a little HNO_3 if any basic salt remains undissolved. The hydrochloric acid HCl and evaporation may be unnecessary in some cases. Filter with a small filter into a 700 c. c. beaker and dilute to 600 c. c.

Precipitate the copper electrolytically. Filter the solution and add from .1 to .5 gram (depending on the amount of sulphur in the copper) of pure dry sodium carbonate $NaCO_3$ and evaporate to dryness in a porcelain casserole. Then heat strongly until the ammonium nitrate NH_4NO_3 formed is volatilized and then cool. Care should be taken not to heat too strongly, as the decomposition of the ammonium nitrate will be too sudden and may cause loss of sulphur.

Add 10 c. c. of strong hydrochloric acid and 5 c. c. of water to the residue and evaporate to dryness on the water bath. Repeat this and then add 1 c. c. of strong hydrochloric acid and 50 c. c. of water. Heat and filter into a small beaker. Heat to boiling and precipitate the sulphur with a slight excess of barium-chloride $BaCl_2$ solution (the

latter should also be hot, as the precipitate of barium sulphate $BaSO_4$ will then settle better). Allow to stand in a warm place until the precipitate is settled, which will require several hours. Filter, wash thoroughly with hot water, dry, ignite, and weigh.

If during the previous filtrations a little lead sulphate has collected on the filters, they must be boiled with a solution of pure sodium carbonate. Filter and acidify the filtrate with hydrochloric acid, boil, and precipitate with barium chloride. Add the weight of $BaSO_4$ found to that previously found and calculate the weight of sulphur by multiplying the weight of $BaSO_4$ by .13734.

96. Oxygen in Copper.—Oxygen is determined by reduction in a current of hydrogen. The sample is obtained by filing a sufficient quantity of chips from a clean test bar of copper with a clean velvet (fine-cut) file. Particles of dirt are picked out with pincers and any small pieces of steel from the file by means of a magnet. About 5 grams of the filings are weighed into a porcelain boat, inserted into a glass or porcelain ignition tube, and ignited in a stream of pure hydrogen gas. They are then cooled in a current of hydrogen and weighed. The loss in weight is credited to oxygen.

97. Gold and Silver.—For anodes, take ½ assay ton and for cathodes from 2 to 4 assay tons of borings and dissolve in nitric acid. Heat to drive off brown fumes, dilute to 500 c. c., let stand for a few hours, and then filter off the gold. Use a rather heavy filter paper.

To the clear filtrate add a very slight excess of a normal solution of sodium chloride (a large excess will dissolve silver chloride). Stir and add 10 c. c. of a saturated solution of lead acetate and thoroughly mix. Then add 2 c. c, of sulphuric acid (1 part of acid to 1 of water). Stir thoroughly and allow to stand for a few hours. When the precipitate is settled, filter and wash to remove copper. The silver chloride is carried down mechanically by the lead sulphate. The filters containing the precipitates of gold,

lead sulphate, and silver are removed from their funnels, wrapped around their precipitates, placed in a 2½-inch scorifier and dried gently on a hot plate, the filter papers burned, and the scorifier set into the muffle to burn off carbon and sulphur. It is well to cover with an inverted scorifier to prevent the fine gold being lost while burning. Now remove and add 5 grams of litharge and 15 or 20 grams of test lead and 1 gram of borax glass. Scorify, cupel, part, etc., as for the ore assay, which was described in *Assaying*. The assays should be made in duplicate and the results checked very closely.

98. Gold and Silver in Refinery Slags.—Take 1 assay ton of the ground sample, 40 grams of sodium bicarbonate, 10 grams of argol, and 10 grams of borax glass. If the slag contains matte, add a loop of iron wire or a couple of tenpenny nails. Fuse, pour, cool, and proceed with the copper button as in copper analyses.

99. Gold and Silver in Slimes.—These metals are determined by the scorification method, taking $\frac{1}{20}$ gram of sampled slimes, ½ assay ton of test lead, and 1 gram of borax.

As the proportion of silver in the slime is large, a little inaccuracy in the results of the assay would make quite an appreciable error in the valuation; therefore, it is necessary to run a check on the assay to determine the loss of silver from volatilization during cupellation. To do this, one assay is run through first. The slag from this scorification is rescorified with ½ assay ton of test lead and the resulting lead button combined with the one previously obtained and cupeled, the cupel showing "feathers." The button of silver containing a little gold is now weighed.

The regular assay is made up in the same proportion as was the check and scorified and the slag scorified with test lead. The lead buttons from these two scorifications are combined as before. To the silver button from the check is added sufficient test lead to bring it up to the weight of the

combined buttons of the assay proper. The two are now cupeled side by side and the resulting buttons weighed. The loss that the check button has sustained is due to volatilization of silver during cupellation. This loss is added to the button of the regular assay, which gives its true weight. Part as usual. The assays should be run in duplicate.

ELECTROMETALLURGY

(PART 3)

ELECTROLYTIC REFINING FROM A COMMERCIAL STANDPOINT

1. Introductory.—In the early days of electrolytic refining, the profits were so great that any one who had the ability to run a refinery did not look at small details of design, etc., provided the process would work somehow. It was not usual in those days for the mining companies selling ore to charge for small quantities of gold and silver in it, as up to that time no process had been found that could profitably extract these metals and consequently copper smelters would have refused to pay for them. The result was that the gold and silver recovered by the electrolytic process were clear profit and often the cost of refining the copper was more than paid for by the precious metals recovered.

This happy state of affairs is now past and mining companies charge the smelters almost full value for the gold, silver, and copper contents, after deducting a small price for the cost of refining. To make a profit, it is, therefore, necessary to work economically, and a badly designed or badly situated plant stands no chance at all of being able to hold its own. The market price of "electrolytic" copper is very little higher than "best selected," and therefore if the anodes do not contain at least 30 ounces of silver or 1 ounce of gold per ton, they will not pay to refine electrolytically.

2. Locality.—In choosing the locality of a refinery, there are many points to be taken into account, and after the best

position—considered from all aspects of the case—has been selected, the design of the refinery must be so modified as to place it upon the best paying basis.

The three big items to be considered are fuel, power, and labor. In addition to this, it should be situated near the mines and smelters and should have cheap freightage to the markets for the finished product. It is hardly to be expected that a locality can be obtained that will have all these conditions favorable, and just which is best under the circumstances will have to be left to the discretion of the expert. A study of the cost sheets submitted and a comparison of the cost of various items there set out, with the probable cost at the locality under consideration, will give some idea as to its suitability or otherwise.

3. Power.—Water-power should, of course, be used wherever obtainable, and if in addition to this the anodes can be produced tolerably free from arsenic, antimony, and bismuth, high current densities of, say, 20 amperes per square foot can be used with corresponding economy, as has been pointed out elsewhere. Of course if power is expensive, the converse of this applies and low current densities must be used. The power then required to refine a ton of copper may be large or small, depending on the current density used, and the current density it is advisable to use is dependent on the price of power.

4. Fuel for Casting Anodes.—Not much economy can be exercised with regard to fuel for casting anodes. All that can be done, if it is expensive, is to take extra precautions to reduce the amount of scrap anode coming from the tanks. Special tanks may be set aside for using up all the large pieces by redrilling and suspending with a copper hook, but since these pieces are liable to hang out of the parallel, greater space must be allowed between anode and cathode and the tanks should, therefore, be of a special size to allow this. *To prevent anodes being cut through at the surface of the solution, which so frequently takes place, they are sometimes*

coated with some insulating varnish along the lines where the solution will come.

5. Labor.—If labor is expensive, every advantage must be taken of labor-saving machines. It is probably to this point more than to anything else that the extraordinary success of American refineries over European is due. Labor is cheap in Europe and refineries have got into a habit of using manual labor where mechanical appliances could be used to advantage.

6. Design of a Refinery.—From what has been said in the foregoing pages, it will easily be seen how impossible it is to lay down any definite rules for the design of a refinery. Much must depend first on the particular conditions that will govern the case and then on the discretion of the designer. The various elements that enter into the design, with their relative advantages and disadvantages, have already been discussed and the student should now be in a position to reason the matter out for himself. However, some guidance in the matter may not be out of place. There are first a number of points to be settled, the chief of which are given below:

1. Output of copper desired.
2. Current density, depending on (*a*) price of power; (*b*) impurities in copper; (*c*) interest on capital.
3. Voltage per tank.
4. Number of tanks.
5. Copper per tank.
6. Current per tank.
7. Diameter of conductors
8. Total cathode surface.
9. Size of electrodes.
10. Distance apart of electrodes.
11. Number of cathodes and anodes.
12. Size of tanks.
13. From the above the horsepower required can be calculated.

Then follow a number of details of construction, and the arrangement of the plant, which can only be considered by

itself. An estimate of the cost of erection will be based upon this, and the interest on capital can be calculated, as previously pointed out. The latter plays an important part in the cost of refining. Knowing the price of labor, power, etc. in the particular district under advisement, the cost of refining can be estimated.

7. Example of Design.—Perhaps the best plan for making the above clear is to take an actual case. It is desired to erect a refinery to turn out 15 tons of refined copper per day. The price of labor, power, etc. is about normal, being neither unusually high nor low. We then get the following figures:

1. Output, 15 tons (30,000 pounds) copper per day.

2. 10 amperes per square foot.

3. .5 volt per tank. This is taken rather high, so as to make allowance for power used round the works for electromotors, lighting purposes, etc. It also makes allowance for any falling off in efficiency of the dynamo.

4. Number of tanks, 300.

5. Copper per tank, $\frac{30000}{300} = 100$ pounds per day.

6. Current per tank: 1 pound of copper is deposited by 15 amperes in 24 hours; therefore, 100 pounds of copper is deposited by 1,500 amperes in 24 hours.

7. Area of conductors: The safe carrying capacity of pure rolled copper is 500 amperes per square inch, therefore $\frac{1500}{500} = 3$ square inches cross-section of conductor.

8. Total cathode surface $= \frac{\text{Total current}}{\text{Current density}} =$ number of square feet of cathode per tank $= \frac{1{,}500}{10} = 150$ square feet.

9. A convenient size for electrodes is $2' \times 3'$.

10. Distance apart of electrodes is rather less than 2 inches, which is about normal.

11. Number of cathodes and anodes: Each cathode is $2' \times 3' = 6$ square feet on each side, or 12 square feet for

(a)

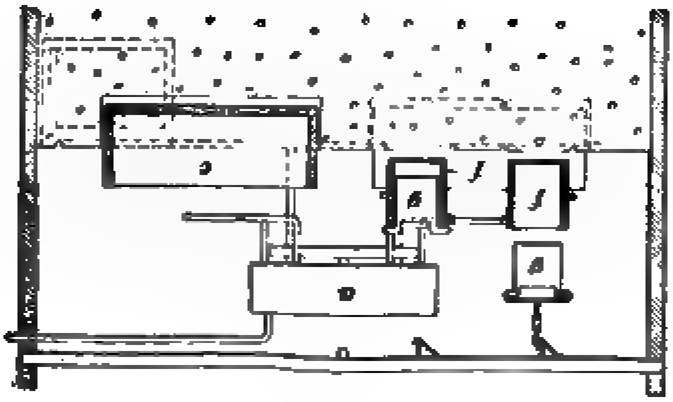


FIG. 1

both sides; 150 square feet required altogether; therefore, $\frac{150}{12} = 12\frac{1}{2}$ (say 13) cathodes required. It is usual to have one less number of anodes, so that the number of anodes required is 12. Total number of electrodes per tank is 25.

12. Size of vats: The length is equal to the number of electrodes times the distance apart, or $25 \times 2 = 50$ inches, say 4′, inside dimension. The breadth and depth are already determined by the size of the electrodes, say, breadth 2 feet 2 inches; depth 3 feet 10 inches, both inside dimensions.

13. Horsepower required:

$$\frac{\text{Current} \times \text{voltage per tank} \times \text{number of tanks}}{746}$$

$$= \frac{1,500 \times .5 \times 300}{746} = 302, \text{ say } 300 \text{ horsepower.}$$

We are now in a position to make a drawing such as is shown in Fig. 1. From what has already been said, this drawing should be self-explanatory; however, the solution is distributed to the baths *f* from the tank *a*, and it then passes from the end tank back through pipe *b* to the sumps *c*. In case one of the tanks leaked, the solution would be siphoned from it into tank *d* until repairs could be made. The liquor is drawn from the tanks *c* or *d* by the pump *e* and returned to the tank *a* unless too foul. In the latter case it may be removed for regeneration by evaporation and crystallization, or sent to the cementation plant. Fig. 1 (*c*) is a section on the line *1* to *4* and shows the precipitating vats *f* and anodes *g*. One anode *g* is suspended above the vat. About 20 per cent. of the tanks should be made 8 or 10 inches higher than above described for the purpose of making cathodes. This is not shown in the drawing.

8. **Cost of Erection.**—The cost of erection will, of course, be somewhat dependent on the price of materials, labor, etc., in the particular locality of the refinery. Below is given an estimate for such a plant as is at present under consideration.

Buildings covering area of 25,450 square feet, requiring 500,000 feet of lumber, at $9	$4,500
Framing 500,000 feet of lumber, including windows, nails, pins, spikes, etc., at $16	8,000
One reverberatory furnace (10′ × 16′ hearth) with anode molds	4,000
One reverberatory furnace (10′ × 16′ hearth) with water bosh, and ingot, and wire-bar molds	4,500
One 36-inch water-jacket blast furnace, for reducing slag, complete with electric motor, fan blower, and 12 slag pots	1,200
Excavations for boiler, engine, and dynamo foundation, 1,200 cubic yards, at $.25 a cubic yard	300
Foundations, 10,000 cubic feet, at $.16 (includes stone, cement, and masonwork)	1,600
Five 72″ × 16′ boilers, at $16 per horsepower, including brickwork	8,000
Air pump and jet condensers	1,390
Two 300-horsepower compound condensing Corliss engines, at $13 per horsepower	7,800
Two 180-kilowatt direct-current shunt-wound generators, at $23 per kilowatt	8,280
700 yards of asphalt flooring, at $.75	525
Circulating apparatus, including air pump	400
Receiving tanks, distributing reservoirs, and launders	245
3,500 feet of 1-inch pipe, 100 1-inch tees, 100 1-inch faucets	220
300 lead-lined tanks, with stringers and brick piers	8,376
Overhead track	600
Silver refinery	3,500
Rectangular conductors, 58,350 pounds, at $.14	8,169
Round conductors, 11,566 pounds, at $.13	1,504
Rolled plates for making cathodes, 3,060 square feet, $\frac{1}{32}$ inch thick, 31,212 pounds, at $.13	4,057
Contingencies, including roustabout labor, blacksmith and pipe-fitter's tools, evaporating tanks, crystallizing tanks, storage sheds, pumps, freight, etc.	5,000
Total	$82,166

9. Cost of Refining.—This will of course vary in different localities, but with a view to showing the relative cost of various items, the subjoined cost sheet is given for the above 15-ton-per-day plant.

Making anodes (including reworking slag)	$51.00
Fuel for electrolysis (cost $4 to $5 per ton)	60.00
Consumption of energy in conductors	44.00
Cost of loss of efficiency	2.70
Treating slimes	13.50
Labor and superintendence	56.00
Maintenance of plant, depreciation reckoned at 10 per cent. on cost	22.50
Oil, waste, light, etc	2.50
Total	$252.20

Cost of refining 15 tons of copper (exclusive of insurance and office expenses) = $16.81 per ton.

THE ELECTROLYTIC EXTRACTION OF COPPER

10. A distinction is made between the extraction and the refining of copper. **Extraction** in the above sense is to obtain the copper direct from the ore, without the intermedial processes of roasting and smelting before refining.

Electrolytic extraction of copper has not met with much success so far, but the great possibilities that this may unfold in the future warrants the insertion here of a short description of what has been so far accomplished. The two most prominent processes are those of *Siemens and Halske* and *Hoepfner*, and they only will be described.

SIEMENS AND HALSKE PROCESS

11. The **Siemens and Halske process** for the direct treatment of copper ores, although not the first of the kind, was the first of any commercial importance. It was

patented in Germany, September 14, 1886, and is applicable to sulphide copper ores. The ore is first calcined slightly to convert the sulphide of iron present into the peroxide, the sulphide of copper remaining unchanged or practically so. The finely ground and calcined ore is now leached in suitable vessels, either tanks or revolving drums, with a solution of ferric sulphate containing free sulphuric acid. The ferric sulphate reacts with the cuprous sulphide of the ore according to the following equation:

$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S$$

The copper appropriates part of the SO_4 of the $Fe_2(SO_4)_3$, forming copper sulphate and reducing the ferric sulphate to ferrous sulphate at the same time the sulphur is set free. Any copper oxide present in the ore formed during the calcining is acted on by the sulphuric acid as follows:

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

or, it may also be acted on by the ferric sulphate according to the equation

$$3CuO + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3$$

12. When the solution is sufficiently saturated, it is filtered and conducted to the depositing tanks or cells and electrolyzed. At first the tanks were divided into anode and cathode divisions by diaphragms, each division containing its proper electrode, but these diaphragms proved inefficient and an entirely different form of tank, shown in Fig. 2, was devised in order to eliminate this troublesome factor.

The apparatus consists of a shallow wooden tank *a* lined with lead and having a false bottom *b*, as shown in Fig. 2 (*b*), which serves as a support for the anode *c*, which is made of retort carbon in the form of plates joined to one another by direct electrical connection; in some cases perforated lead plates covered with fragments of retort carbon have been successfully used. Upon the anode is placed a filter made of felt or some other suitable material. This retains the solution around the anodes. The remaining upper portion

of the box serves as the cathode division. The cathodes are of peculiar construction, being wooden drums *d*, Fig. 2 (*a*), covered with copper *k* to give them a conducting surface.

(*a*)

(*b*)

(*c*)

FIG. 2

These drums are suspended at either end by the conductor *e*, Fig. 2 (*b*), with which the conducting surfaces are in electrical connection, and are revolved slowly by means of pulleys *f*

and belts *g*. The solution, which has been upon the ore and is now heavily charged with copper and ferrous sulphates, is conducted into the cathode division in a continuous stream, the revolving drums being completely submerged. It passes through the filter into the anode division and under the false bottom, from which place it is led away through the pipe *h*.

13. The electrical current enters the bath through the anodes by means of insulated conductors, passes through the electrolyte, and deposits copper upon the metallic surface of the cathode drums. The fresh solution entering constantly at the cathodes keeps up the supply of copper, which, being deposited, leaves the weak solution to pass over the anodes and out through the pipe. The anion SO_4 migrates to the anode, where it unites with ferrous sulphate and converts it into ferric sulphate. The solution of ferrous sulphate passing out free from copper is ready for leaching fresh ore and to pass again through the same series of operations. The difference of potential necessary for this purpose is reported to be .7 volt and a current density of 1.5 amperes per square foot.

There have been some other later improvements in this apparatus, principally in the form of anodes and cathodes and in the general arrangement of the plant, the anodes being composed of a series of carbon bars held in position by lead castings and the cathodes simply wooden plates covered on the under sides with sheet copper upon which the deposit is received.

HOEPFNER'S PROCESS

14. As a process for the electrolytic treatment of copper sulphide ores without any intermediate refining, the **Hoepfner process** is one of the most interesting. It was invented by C. Hoepfner and was patented in Germany, March 1, 1888. It is often called the **cuprous chloride process** and is manipulated in general as follows:

The finely ground ore is leached in suitable tanks or revolving drums with a solution of cupric chloride $CuCl_2$ in a solution of common salt $NaCl$ or calcium chloride $CaCl_2$. The leaching is done in two stages. First, the solution is conducted upon ore that has already undergone one treatment in order to remove any copper remaining in it. After a sufficient length of time the solution is drawn off to another vat or drum containing fresh ore. Here the cupric chloride is completely reduced to cuprous chloride $CuCl$, the solution then containing twice as much copper as before; the reaction taking place according to the following equation:

$$CuCl_2 + CuS = 2CuCl + S$$

The contents of the lixiviation tanks are pumped out, passed through filter presses, and the residue washed. The solution now contains impurities in the form of other metals, which were dissolved at the same time as the copper. Principally among these are silver, lead, iron, arsenic, antimony, and bismuth. These metals must be removed to insure a deposit of pure copper. Silver is removed by the addition of finely divided copper, upon which it is deposited. Lead chloride is precipitated upon cooling the solution, it being quite insoluble when cold. The other substances are precipitated by means of lime or copper oxide. The now comparatively pure solution is ready to be electrolyzed. It flows into the baths in two separate streams, one to the anodes and the other to the cathodes.

15. The electrolytic tanks are constructed of wood or other suitable material and are divided into anode and cathode compartments, separated from one another by means of porous diaphragms. The streams of regenerated solution flowing to the electrodes are alike when they enter the tanks, both containing the same proportion of cuprous chloride. The copper in the cathode solution is deposited on the cathodes as it passes successively from one to the other and the solution finally passes out more or less impoverished of copper. The amount of copper in the anode solution

remains the same, but that does not imply that its condition is the same as before. The copper entered in the state of cuprous chloride $2CuCl$. During the electrolysis, for every 2 atoms of copper deposited 2 atoms of chlorine are liberated and migrate to the anode, where they immediately unite with a molecule of cuprous chloride, converting it into 2 molecules of cupric chloride, according to the reaction

$$2CuCl + 2Cl = 2CuCl_2$$

The two streams of solution after passing through the baths are united in a suitable receptacle and the resulting solution is then in condition to be used again on fresh ore, it containing the same amount of copper as at first in the original state of cupric chloride.

16. Advantages of this Process.—Theoretically and practically there are points about this process that are very much in its favor; the copper being in a cuprous state requires just one-half the current for its deposition as when in the cupric state. One ampere-hour deposits 1.18 grams of cupric copper and 2.36 grams of cuprous copper.

If there were no cuprous chloride at the anode, free chlorine would be liberated and the electromotive force required for the electrolysis would be 1.8 volts; but the cuprous chloride, as has been shown, combines with the chlorine that appears at the anode, and in doing this creates an electromotive force in a direction favorable to the process, so that practically a difference of potential of but .8 volt is required between electrodes for the electrolysis.

The chloride solution has a high efficiency as a solvent for the valuable metals, its dissolving power for copper being especially high. It is stated by Hoepfner that for every ton of coal required for heating, pumping, deposition, etc., 1 ton of copper can be deposited.

17. Disadvantages of the Process.—Owing to the heat necessary for dissolving the copper, the solution becomes heavily charged with iron. The cost of very fine crushing is excessive.

The diaphragm problem has proved a difficult one, because suitable and at the same time inexpensive diaphragms have not as yet been obtained. The latter problem seems to be solved in the Cohen process by doing away with diaphragms in an especially constructed bath in which the cupric chloride formed at the anode, having a higher specific gravity than the chloride solution, settles at the bottom, where it forms a distinct layer, into which the anode extends. The cathode is short and does not reach the highest level of this layer, which is kept from accumulating by a siphon discharge. It is quite probable that the obstacles to this process will be overcome to a great extent.

THE ELECTROLYTIC REFINING OF SILVER OR DORÉ BULLION

18. The electrolytic methods for refining silver, although not universally employed, are steadily increasing in favor, owing to their cheapness and the remarkable purity of the product obtained. The metal is particularly well adapted to electrolytic refining, and especially to those methods that depend on the solution of the silver at the anode and its redeposition at the cathode.

The processes for the recovery of silver from its alloys may be divided into two distinct classes. First, that in which the silver is but a small percentage of the metals of the alloy and when the latter is electrolyzed for the deposition of the principal metal. The silver and gold in such instances are not dissolved in the electrolyte, but are separated out at the anode in an insoluble form, called slimes, mud, or residues.

19. The recovery of silver and gold in this way, when alloyed with copper, was quite thoroughly discussed in the chapter on the refining of copper. Electrolytic methods are also used in the recovery of silver in the refining of lead bullion by the Roessler-Edelmann process. The crusts

produced by the Parks process contain too much lead to give satisfactory results by electrolytic methods. The silver and gold in these residues are not pure, and must be further refined and parted by other methods, either chemical or electrolytic. The former methods have already been taken up, while the latter will be considered in this chapter.

20. Under the second head come all processes using impure silver or doré bullion, that is, fine silver bullion carrying considerable gold, as anodes, the silver going into solution and being deposited at the cathodes. The gold and some of the other impurities remain insoluble.

Copper goes into solution, but is not deposited in the presence of silver if the proper conditions are maintained. Such processes are strictly direct refining and the product is practically pure silver. The success of any process for the treatment of the precious metals depends to a great extent on the rapidity with which the metals can be treated, and thus prevent their retention at the refinery for any great length of time, as the interest on such valuable metals as gold and silver is a factor that must always be considered. Fortunately, very high current densities can be used in the treatment of silver, and as the rate of deposition is in direct ratio to the strength of current, it follows that the refining proceeds rapidly.

THE MOEBIUS PROCESS

21. The simplest and most efficient process that is in use for the electrolytic refining of silver and the only one that need be described here is that invented by B. Moebius. It was first patented in Germany in 1884 and in the United States in 1885. The early form of apparatus has recently been somewhat modified, making the process continuous but without changing it in principle.

Both forms are in successful operation in Europe and the United States and are fully described below.

22. The Old Moebius Process.—The form of the electrodes and the general construction of the apparatus used do not differ essentially from that of an electrolytic copper refinery, but it is on a much smaller scale, corresponding to the smaller quantity of metal treated and also to the increased rate of treatment.

The tanks used are about 11 feet long, 2 feet wide, and 20 inches deep (inside measurement). They are built of 2-inch plank very carefully joined together. Each tank is divided into seven compartments or cells by means of wooden partitions, each cell being 2 feet long by 18 inches wide. In some refineries these cells are simply painted with tar, in others they are lined with sheet rubber to protect the wood from the action of the acids and to prevent loss from leakage. In each cell are suspended three rows of anodes and four of cathodes.

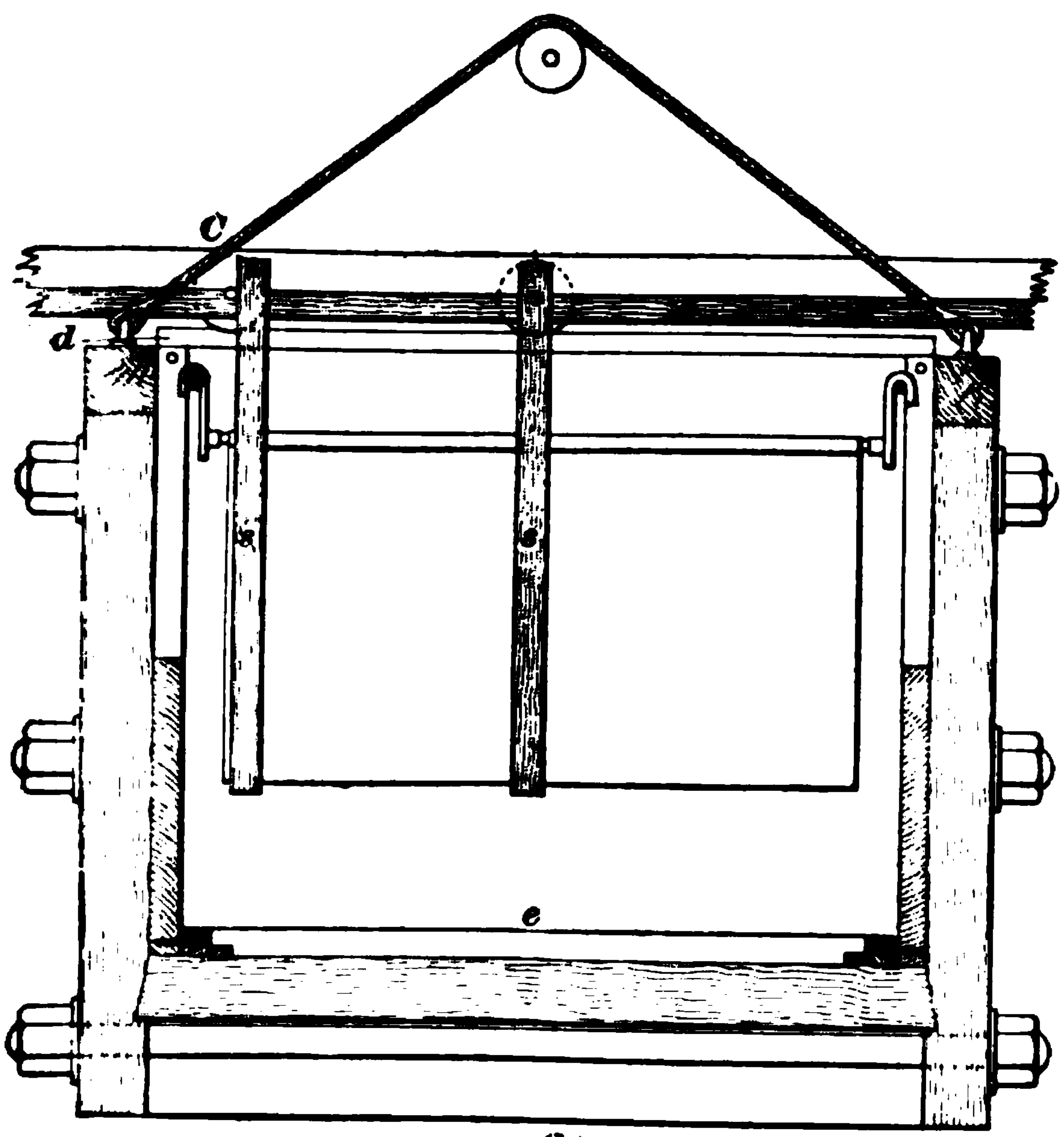
23. Anodes.—The anodes of doré bullion, which have been refined by cupellation until they contain not more than

FIG. 8

from 2 to 5 per cent. of impurities (lead, copper, and bismuth), are cast directly from the cupels into flat plates 18 inches

F

FIG. 4



(b)

long by 10 inches wide, by ¼ to ⅜ inch thick. Various methods are used for suspending anodes in the cells. In one American plant three lugs are cast on a long side, in which are punched holes to receive wires. They are depended in the solution by the wires from copper rods 28 inches long.

In a large German plant, a single lug is cast on one end of the anode *a*, as shown in Fig. 3. The plates arc suspended from a metal frame *B* by means of the double wire hooks *c*, five anodes being suspended in a row and three rows to a cell. Each row is enclosed in a cotton or linen bag to catch the gold. Alternating with the rows of anodes are cathodes of rolled silver suspended from copper rods. The electrical conductors *D* are placed along the upper rim of the tanks, so that the cells are electrically in series. These conductors are copper, bronze, or brass bars and not only serve to conduct the current to the cells, but also support the weight of the electrodes, whose supporting rods rest on the conductors. The anode bars rest at one end directly upon the positive conductor, while the opposite end is insulated from the negative conductor *E*. The cathode bars are in contact with the negative conductor and are insulated from the positive conductor in a like manner; thus the electrodes are in multiple with reference to one another.

24. Depositing Silver.—With the high-current density used, the silver is deposited rapidly as beautiful, brilliant, coarse crystals, which if not removed from the cathode would soon extend across to the anode and short-circuit the plates. To prevent this, a mechanical device is used that scrapes off the crystals as fast as they are formed. This consists of wooden slats *s*, shown in Fig. 4, attached to a frame *b*, which is made to slide backwards and forwards on wheels *C*, running on a track *d*. These scrapers are arranged in pairs, so as to straddle the cathode, there being two pairs to a cathode.

25. Below the electrodes and covering almost the entire bottom of each cell is a wooden tray *e* with a bottom made of slats hinged at one end and fastened by wooden dowels or pins at the other. Over this slat bottom is spread a coarse

cloth (linen or asbestos). This tray is fastened to the frame that carries the electrodes and scrapers, so that the entire apparatus can be removed from a tank at once by means of a hoisting arrangement.

The silver crystals falling from the cathodes are caught upon the cloth bottoms of the trays. At proper intervals (once every 24 hours) the frames carrying the trays, etc., are hoisted out and the silver crystals dumped out by dropping the hinged bottom. The apparatus is then lowered back and the operation continued.

26. The electrolyte used is a weak solution of copper and silver nitrates, acidified with nitric acid. At first the proportion of copper in the solution is small, but as the copper in the anodes is dissolved and not redeposited, it gradually accumulates in the solution; as much as 5 per cent. of copper may be present before there is any danger of its being deposited with the silver, provided the solution is sufficiently acid.

Copper in dissolving to cupric nitrate requires nearly $3\frac{1}{2}$ times as much nitric acid as does the same weight of silver. When the anode bullion is high in copper, nitric acid must be added more frequently than when very little copper is present.

The tanks are filled with a weak acidulated solution of silver nitrate as electrolyte, or if desired, the work may be begun with very dilute nitric acid. As soon as the above described apparatus has been put into the tank, the electrical connections may be completed. The maintenance of a constant current density is of far less importance in this process than in most electrolytic operations. Especially at the outset or as long as the solution contains but little copper a very high current density is permissible; it may exceed 29 amperes per square foot. In the course of electrolysis, the copper from the anode, which sometimes contains as low as 95 per cent. of silver, gradually accumulates in the bath, so that the proportion of copper present will on the average be higher than that of silver. The copper may

amount to 4 or 5 per cent. and the silver to .5 per cent. when from .1 to 1 per cent. of free nitric acid is present. It is essential that as the percentage of copper increases, the proportion of free nitric acid also be raised; and the current density should be lowered to about 19 amperes per square foot. The electromotive force required will usually vary from 1.4 to 1.5 volts per cell.

27. The following description of the plant of the Pennsylvania Lead Company, of Pittsburg, Pennsylvania, is taken from an article by Mr. George Famce in the Journal of the Franklin Institute of October 5, 1895.

The primary object of the company was the production of refined lead suitable for the manufacture of white lead. Practically all the lead now produced west of the Mississippi valley carries more or less silver or gold. In refining the lead these impurities must be removed. Therefore, treatment of gold and silver becomes an essential part of the business of lead refining. The silver and gold are taken out by means of zinc, which when mixed with the molten lead combines with the precious metals and carries them to the surface in the form of a crust, which is skimmed off and is subjected to a high heat to distil the zinc. The alloy of lead, silver, and gold now left is cupeled to remove the lead from the silver and gold.

The silver is refined on the cupel until it contains not over 2 per cent. of impurities (lead, copper, and bismuth). If more impure silver is treated, there is more or less bother with accumulations of copper and lead in the solutions, with consequent large amounts of by-products and increasing difficulty in turning out fine product. When the silver has attained the proper degree of purity, it is cast from the cupel into flat plates about 18 inches long, 10 inches wide, and ½ inch thick, weighing from 425 to 475 ounces troy (about 30 pounds avoirdupois).

28. These silver plates form the anodes in the electrolytic operations. Each plate has three projections or lugs on one of the long sides, in which holes are punched to

receive the wires that suspend the plate in the solution. The three supporting wires, which are $\frac{3}{16}$ inch in diameter, are attached to a copper rod 28 inches long and $\frac{1}{2}$ inch in diameter, and then the plates are ready to be placed in the tanks.

29. The ninety-eight cells are arranged in sets of seven, each set being styled a tank. These tanks are made of California redwood plank, joined together very carefully. The bottom is lined with sheet rubber. Each tank is 11 feet long, 24 inches wide, and 20 inches deep (inside measurement), each separate cell being 2 feet long by 18 inches wide.

30. The electrolyte is a solution of silver nitrate and copper nitrate in dilute nitric acid. The acid present is only from $\frac{1}{2}$ to 1 per cent. of the solution, merely enough being used to prevent the deposition of the copper. The consumption of acid is about 1 pint every 24 hours for each bath. The current is conducted to the baths through rods $\frac{5}{8}$ inch in diameter. The rods connecting the tanks are so arranged that any one or any number of the tanks may be left out of the circuit if desired.

31. Silver Cathodes.—The cathodes are thin sheets of fine silver 13 in. $\times$ 20 in. $\times$ $\frac{1}{32}$ in., weighing 50 ounces troy, or $3\frac{1}{2}$ pounds avoirdupois. These cathodes are rolled in the machine shop of the company from their own silver. In each bath four of these cathodes are suspended, alternating with three anodes. The distance between anodes and cathodes is about $1\frac{3}{4}$ inches. The rods that support the cathodes and anodes rest on the main conducting rods, which are arranged horizontally along the sides of the tanks. On one side of the bath, when the current enters the anodes, the ends of the cathode wires are insulated by rubber; on the opposite side, the ends of the anode rods are insulated, while the cathode rods are in direct contact with the conductor.

32. The current from the dynamo has an intensity of 180 amperes. It enters the bath through three anodes and

is therefore divided into three parts, each with an intensity of 60 amperes. It passes out at each side of each anode through the solution to the cathodes, so that the intensity of the current through the solution is 30 amperes. These divisions of the main current after they pass through the cathodes are reunited in the main rod and carried to the next bath. The cells are arranged in series, the whole current passing through each bath.

Each anode is suspended in a muslin bag, which serves to collect the undissolved metals, which fall in the shape of a black slime. The metals thus caught are all the gold and bismuth, the greater part of the lead as peroxide, together with some silver and copper.

33. Below this system of anodes, cathodes, and bags, a piece of cloth is stretched on a box-like frame. The deposit of silver is scraped from the cathodes by wooden "brushes" and is collected upon the cloth. The brushes straddle the cathodes, hugging close to each surface without touching. They are kept moving to and fro by machinery and brush off the silver as fast as it is deposited on the cathodes, thus preventing short-circuiting. They also keep up a constant agitation of the liquid and prevent, to a large extent, polarization and the tendency of the solution to settle into layers.

The principal points covered by the patents of Mr. Moebius relate to these mechanical stirrers and the bags for collecting the gold slimes.

34. Current Density for Silver Deposition.—Now suppose that there are 10 tanks or 70 baths. The dynamo is made to generate a current of 180 amperes. The voltmeter shows an E. M. F. of about 90 volts. Then by Ohm's law $R = \frac{E}{C}$, it appears that the resistance of the circuit is $\frac{1}{2}$ ohm, or about .007 ohm for each bath. The work absorbed by this current is

$$W = \frac{180 \times 90}{746} = 22 \text{ H. P.}$$

The total cathode surface per bath is 10 square feet. The current being 180 amperes, the density of the current will be about 18 amperes per square foot of cathode surface.

35. The current in its passage through the solution decomposes the nitrate of silver. Silver is deposited on the cathodes in the shape of dazzling white coarse crystals and nitric acid is formed. This acid attacks the anode, dissolving silver and restoring nitrate of silver to the solution. The nitric acid also dissolves the copper and some of the lead and oxidizes the bismuth and the rest of the lead, making products that remain undissolved in the bags.

36. Rate of Deposition.—It has been mentioned that the density of the current is 18 amperes per square foot of cathode surface. This is high compared with the density used in copper refining and is the cause of the loose crystalline deposit, as with a low current density the deposit tends to become cohesive. In the case of silver, this crystalline structure is of advantage, as the silver can easily be brushed off and collected at frequent intervals. If it were deposited in a cohesive coating, either a far greater quantity of silver would need to be carried in stock, which would unduly increase the interest charges, or one would have to be continually remelting old cathodes and making new ones, which would be expensive. A current of 1 ampere will deposit from a solution of silver nitrate 1.12 milligrams of silver per second; a current of 180 amperes, therefore, will deposit 201.6 milligrams per second.

37. According to the second of Faraday's laws, the same current will deposit equal amounts simultaneously from each of the seventy baths; consequently, this current would deposit 14.11 grains per second in the whole series. This amounts to a deposition of 50.8 kilograms per hour, that is, 1,219.28 kilograms per day, or 39,205 troy ounces. As the horsepower expended to deposit 50.8 kilograms per hour is about 22, it follows that each kilogram of silver deposited

consumes about $\frac{1}{2.3}$ horsepower per hour; that is, about 4.66 pounds silver are deposited per horsepower per hour.

Although, theoretically, the seventy baths should deposit 39,205 ounces per day, in practice this yield is not obtained for several reasons:

1. The anodes must be drawn out of the bath for the purpose of cleaning up the gold and silver. This consumes considerable time each day.

2. Shorter interruptions of the deposition are necessary for replacing anodes, cleaning connections, examining insulations, etc.

3. With the small machine used, which is not quite large enough for the work put upon it, constant vigilance is necessary to keep the current up to 180 amperes throughout the 24 hours, and of course any lowering of the intensity of the current means a proportionate decrease in the output.

38. The actual working results day in and day out will average 33,000 ounces per day for the seventy baths. It would be possible for a short time to deposit in the whole plant from 45,000 to 50,000 ounces per day; but in the long run it will be found necessary to keep one-seventh of the tanks under repair all the time.

The labor required in the process is slight. A carpenter is employed constantly in repairing and rebuilding tanks, making brushes, boxes, etc. A mason and machinist are needed about one day per week for other repairs. Three men in the daytime and one at night are all that are required to do the work, which consists of melting the fine silver and cleaning up, preparing the anodes, and placing them in the bath at the proper time, clearing up and refining the gold slimes, melting scrap silver, keeping connections clean and insulations perfect. Each tank is cleaned of silver every other day and of gold once a week. A full-sized anode is dissolved in about 2½ days.

39. Fineness of Deposited Silver.—The deposited silver as soon as it is taken from the tanks is washed

thoroughly with hot water, in order to rinse out the copper-bearing solution. It is then melted down in a large plumbago retort, which is capable of holding 18,000 ounces, or about 1,200 pounds avoirdupois. The fuel used is natural gas. Each retort melts on the average about 5 tons before breaking.

40. The fineness of the silver produced is 999—often 999.5. Indeed, it would require no effort to produce silver 999.5 fine regularly, if it were of any advantage. By repeated washing it is possible to obtain almost absolutely pure silver. Silver has been furnished to the mint as fine as 999.85. The gold slimes are melted, granulated, and parted by acid. The resulting gold is from 996 to 998 fine.

41. The electrolyte is of a beautiful green color, due to the presence of 4 or 5 per cent. of copper. It also contains a small percentage of lead. As has previously been stated, when these three metals are present in the nitric solution, the silver, being the most electronegative, is deposited before the others.

42. So long as the copper and lead are not present in too large quantities and so long as a proper amount of acid is used, the silver will be deposited in a state of absolute purity. As the copper and lead accumulate to a dangerous degree, it becomes necessary to withdraw part of the solution and after throwing out the silver with salt to precipitate the copper and lead.

With large percentages of copper and lead in the anodes, it was found at these works impossible to obtain silver fine enough to ship to the mint.

Mr. Moebius in his Mexican plants has, it is said, treated bullion carrying 30 per cent. to 40 per cent. of copper. But it should be noted that the Mexican mint is not as strict as the United States mint and is satisfied to take silver containing 10 per cent. of copper.

43. **The New Moebius Process.**—As previously stated, the **new Moebius Process** does not differ in principle from

the old, the difference being in the form and arrangement of the electrodes and in the mechanical arrangements whereby the deposited silver crystals are removed from the tanks as fast as formed, thus increasing the capacity of the tanks, as no delays are necessary for clean-up silver, as was the case in the old process.

(b)

Fig. 5

(a)

In Fig. 5 (*a*) and (*b*) is shown the construction of the tanks used. The tank *a* is about 14 feet long, 16 inches wide, and 7 inches deep, built of 2-inch pitch-pine plank and coated with an acid-proof paint. The anodes, which are plates *b* about 15 in. × $3\frac{1}{2}$ in. × $\frac{1}{2}$ in., cast from doré bullion, instead of being suspended vertically, as in the old process, are placed horizontally in the anode trays *c*. These trays have perforated bottoms that are covered by some kind of porous diaphragm. They are shallow, 18 inches square by 1 inch deep, but are deep enough so that the anode plates are completely submerged in the electrolyte. Electrical connection is made with the anode plates by means of the contact arm *d*, one end of which is attached to the negative conductor *e*. The opposite or contact end formerly had a platinum tip *f* and above this was a rubber jacket *g*,

Fig. 6, to protect the wire from the action of the electrolyte.

The action of these arms are illustrated in Fig. 5 (*a*). The cathode *h* is in the form of an endless belt, about 26 feet long by 15 inches wide. Originally this belt was of rubber faced on the outside with silver. More recently, however, bands of pure silver $\frac{1}{32}$ inch thick have been used. These are oiled on the outside to prevent the deposition of silver on them.

FIG. 6

The belt is supported at each end by the hard-rubber rolls *i* and *j*, the latter being revolved slowly by a chain gear *k*, thus giving the belt a speed of about 3 feet per minute.

The electrical connections are made by means of the brush *l* with the negative conductor *e*. The crystals are transferred to the elevator belt *m* and carried outside the tank, where the scraper *n* knocks them into the receiving tray *o*. After they are drained they are ready for the melting pot. With this belt form of cathode the electrodes may be very close together without any danger of short-circuiting, as the crystals cannot accumulate and bridge across; the resistance of the cells is, therefore, very much reduced.

44. The electrolyte ordinarily used is an aqueous solution of sodium or potassium nitrate sufficiently acidified with nitric or sulphuric acid to keep some of the silver and all of the copper in solution. This solution is a very good conductor of electricity.

The current densities used and the precautions necessary to be taken are the same as in the old process. The surface of the silver belt upon which the deposition takes place should be frequently coated with graphite composition to prevent the deposited silver crystals adhering to it. It is necessary to take this precaution, as otherwise the belt will get brittle and crack and be ruined in a short time. When

the operation of a tank is suspended for a time, the belt should be removed, as the dilute acid in the electrolyte will gradually corrode and finally perforate it.

45. This process has been installed in a number of the large refineries in the United States, among which are the Guggenheim Smelting Company, Perth Amboy, New Jersey. At the time of installation this silver-refining plant consisted of forty-eight electrolytic tanks, each 14 feet 3 inches long by 16 inches wide by 7 inches high, arranged in eight groups, each group consisting of six tanks. The tanks of each group were placed in two tiers, three tanks high, one above the other, with a space of 1.5 feet between each pair of tanks. The top of the upper tank is 5.5 feet from the floor. The groups are separated by 4-foot aisles. The individual tiers of a group are separated by a floor space of 1 foot 3 inches.

The refinery room containing the tanks is 40 feet wide by 80 feet long, having a cement floor sloping so as to drain into a cement pit 30 feet long by 4 feet wide by 4 feet deep. The electrolyte is prepared in this pit by dissolving granulated silver in nitric acid and adding the proper amount of sodium and copper nitrates. The solution used normally contains about .1 per cent. of free nitric acid, from 4 to 5 per cent. of copper, and 12 ounces of silver per cubic foot.

Sulphuric acid is added occasionally to precipitate any lead that may have become dissolved in the electrolyte. The consumption of nitric acid is about 1¼ pounds for every 1,000 ounces of doré bullion parted.

46. Each tank contains six anode frames, 18 inches square and 1 inch deep, over which are stretched muslin diaphragms. The frames are divided into four sections by strips, an anode being placed in each section. These doré anodes, running about 980 fine in silver and from 3 to 8 fine in gold, are cast in plates 15 in. × 3½ in. × ½ in. The cathode belt is ½ inch below the anodes and consists of a belt

of rolled silver 31 feet long by 15 inches wide by $\frac{1}{16}$ inch thick. The upper, or outer, side of the belt is painted with graphite composition once a week during the first month to prevent the silver crystals adhering to it. The belts travel at a speed of about 3 feet per minute over gutta-percha rolls. The power required for driving the chains and gearing moving the belt is about 3 horsepower.

47. The circulation is affected by overflow from one top tank to the next across and down. The lowest tank empties into the collecting reservoir previously mentioned. From the collecting reservoir an acid-proof pump forces the solution into the distributing tank, from which the electrolytic tanks are supplied with fresh solution.

The electric power is supplied by a generator having a capacity of 300 amperes at 150 volts, but only 220 amperes at 90 volts were being used for the deposition of 24,000 ounces daily.

48. The E. M. F. required per tank is from 1¼ to 2 volts. Platinum-tipped contacts are used to make electrical connections with the anodes. The fine silver crystals scraped from the belt drop through a closed chute into a bin placed at the end of each set of tanks. They are washed in a double-bottomed vat by exhausting the air underneath the false bottom and while still moist are charged into graphite retorts and melted into 70-pound bricks.

Usually not even a trace of gold is found in the silver. The anode residue contains besides gold considerable peroxide of silver, bismuth, lead, and antimony. It is washed, dried, and melted in a graphite retort. Most of the impurities are removed by skimming off the slag. The metal is then either alloyed with silver and granulated for final parting or it is cast into bars and again subjected to electrolysis to concentrate its contents in gold. The granulated alloy containing about 3 parts silver to 1 part gold is parted with nitric acid in the usual way. The nitrate of silver is added to the silver electrolyte and the gold cast into bars.

49. In each tank are deposited about 600 to 700 ounces of silver every 24 hours. The entire plant requires an attendance of but two or three men per shift, so that the running expenses are very small. It has been estimated that the cost, exclusive of general expenses, superintendency, and royalty, for parting 30,000 ounces of doré bullion is about $38.50, or ⅛ cent per ounce.

The advantages of the Moebius process are the low cost of the plant and parting (the apparatus for a plant having a refining capacity of 30,000 ounces of doré bullion in 24 hours need not cost over $6,000 if the cost of the engine and dynamo are not included); the total absence of noxious gases, except during the acid treatment of gold residues; the small amount of labor and chemicals required; the cleanness and rapidity of working. From the fact that practically no by-products are produced, the chances for loss of metal are reduced to a minimum.

ELECTROLYTIC EXTRACTION OF ZINC

50. Introductory.—The extraction of zinc from its ores by chemical methods and the subsequent deposition of the metal by electrolysis has not been brought to the high degree of perfection that the amount of labor and study put upon this subject might warrant. Several processes have appeared to promise much, but for the most part they have not proved in practice to be entirely successful for either technical or financial reasons. Great results, however, are expected in this branch of work in the near future, and the subject of electrometallurgy would not be completely dealt with unless some study were given it.

51. There are two causes that have been instrumental in the non-success of the electrolytic extraction of zinc. First, the low price of zinc; and since the very pure metal that is obtained electrolytically commands no higher price than the commercial article, the margin of profit is rather uncertain. Second, it is difficult to deposit zinc electrolytically in a hard

and uniform condition. The deposit is apt to be spongy or soft and in a condition unfit for melting.

There are, however, a few processes in various parts of the world that are said to be, or have been, in successful operation, and many special processes that may, with proper management, be developed and established on a profitable working basis.

52. The subject of electrolytic treatment of zinc ores is deserving especial attention, because vast deposits of ore exist, which consist of a mixture of zinc sulphide (blende) and lead sulphide (galena). These carry considerable quantities of silver and have up to the present baffled all attempts at treatment by ordinary metallurgical methods. If the electrolytic process could be made to work as well in practice as it does in the laboratory, the profits would be enormous, since these ores can be purchased at a very low rate.

If it is attempted to treat these zinc-lead sulphides as a zinc ore and distil the zinc off in the ordinary way, leaving the lead and silver behind, the lead oxide or sulphide fuses and quickly destroys the retort. On the other hand, if the mixed sulphides are treated as a lead ore, the zinc volatilizes in the lower part of the blast furnace and condenses as oxide in the upper part, very soon choking the furnace. Mechanical separation by crushing and jigging is almost impossible, owing to the extremely intimate mixture of the two sulphides.

This explanation is introduced for the purpose of impressing upon the student the great advantage that the electrolytic process possesses in comparison with any other metallurgical method. It must be borne in mind that the electrolytic process must look to the treatment of these rebellious ores for its chief source of profit and not to the treatment of ordinary zinc ores, which can be cheaply treated by other methods.

53. Leaching the Ore.—In order to obtain the zinc contents of the ore in a solution suitable for electrolysis, the

ore must be leached after a preliminary roasting if necessary with a solution of chemicals that will convert the insoluble zinc compounds into soluble forms. Many different substances and solutions have been used. The different methods of doing this may be grouped under two heads: First, treatment with acid solutions, including the treatment with acid salts; second, treatment with solutions of alkalies.

TABLE SHOWING SOLUTIONS SOMETIMES USED

Acid Solutions	Alkaline Solutions
Sulphuric acid H_2SO_4	Ammonia NH_4OH
Hydrochloric acid HCl	Caustic potash KOH
Acetic acid CH_3CO_2H	Caustic soda $NaOH$
Sulphurous acid $SO_2 + H_2O$	
Ferric sulphate $H_2SO_4 + Fe_2(SO_4)_3$	
Ferric chloride $HCl + FeCl_3$	

54. In the acid treatment, the object is usually to get the zinc into solution as a sulphate or chloride unadulterated with iron and other injurious elements. The condition of the zinc ore should be such that the leaching may be complete. Oxidized zinc ores (the oxide and carbonate) do not require roasting; however, the sulphide or the mixed blende and galena must be roasted previous to leaching in order to convert the difficultly soluble blende into a more soluble form. If the zinc is to be treated as a sulphate, the roasting is conducted in such a way as to convert as much of the zinc sulphide as possible into zinc sulphate, which reduces the cost of the acid required in the leaching solution. If the zinc is to be converted into the chloride, a chloridizing roast with common salt is usually resorted to.

Among the many processes that have been proposed and which depend on the use of acid solutions, the following are the most noteworthy.

55. Luckow's Process.—Luckow was the first to patent a process for the deposition of zinc electrolytically that was of any technical importance. In his process, patented in 1880, the zinc was deposited from a solution of zinc chloride or sulphate, using insoluble anodes, and at the same time passing a stream of sulphur dioxide SO_2 into the electrolyte. The SO_2, being a strong reducing agent, converted the anions Cl_2 or SO_4 in the presence of water into HCl or H_2SO_4 for the purpose of reducing polarization, according to the following equations:

$$Cl_2 + SO_2 + 2H_2O = 2HCl + H_2SO_4$$
$$SO_3 + H_2O = H_2SO_4$$

It is seen from the above equations that the quantity of acid present is rapidly increased. In fact, the amount is doubled after each treatment, so that it must be soon disposed of. Although this process has not been adopted, it is of interest as being the first important step in the right direction.

56. Letrange's Process.—Letrange brought out a process a few years later than Luckow for the treatment of zinc ores. His plan was to roast sulphide zinc ores very gently, so as to convert most of the sulphide into sulphate. This sulphate was to be dissolved out with water and the resulting solution electrolyzed. The sulphuric acid thus set free was used to dissolve zinc carbonate (smithsonite) or oxide. The leaching was to be done in a series of masonry basins, to which the acid solution was conducted by pipes. As soon as the leaching was complete, the solution of zinc sulphate was to be conducted to a reservoir in which it could be purified, after which it was passed into the electrolytic tanks. The solution of zinc sulphate passed in at the bottom of the tanks, the zinc was deposited, and the liberated sulphuric acid passed out at the top.

57. In case very pure zinc oxide was to be treated, both the leaching and deposition could be done in the electrolytic tank. The zinc oxide or smithsonite, mixed with carbon to make it a conductor, was placed in one compartment

with the carbon anode, and the zinc solution and the cathode of brass or zinc in the other, the two compartments to be separated by a porous partition.

The chief difficulty with this process was that the zinc was not deposited as a reguline metal, but in a more or less spongy form, which fell to the bottom of the vat and was there redissolved by the free acid. In fact, the free acid, which is a necessary and increasing product of the reaction, was generally a nuisance, and when in any quantity would even attack the cathode itself.

The zinc was deposited on the cathodes in sheets from .16 to .2 inch thick. These sheets were then stripped from the cathodes.

This process was tested on a large scale at St. Denis, France, but was not a practical success.

58. Nahnsen's Process.—Nahnsen has improved this process. He uses for an electrolyte a mixture of a solution of zinc sulphate and an alkaline sulphate, the exact composition of which is, however, kept secret. His process is somewhat as follows. The roasted blende is treated with a hot acid solution as it comes from the vats, extracting the zinc from them. This zinc solution is neutralized, clarified, and heated with zinc dust to precipitate any electronegative metals that may be present. It is then ready to go to the electrolytic tanks.

In the electrolytic tanks the action is very much the same as in the Letrange process. The solution passing out of the tanks is used again in leaching fresh ore.

It is essential that the zinc-sulphate solution be free from iron. To make sure of this, the solution is passed over ores containing increasing quantities of zinc oxide, which precipitate the iron as ferric hydroxide.

Zinc is said to have been obtained by this process in dense plates .8 inch thick, having a purity of 99.9 per cent. But in 1902 it had not come into general use.

59. Lindemann's Process. — In this process zinc is deposited in a very pure state from a solution of zinc

sulphide ZnS in suspension. The sulphide of zinc is produced by precipitation from a solution of sulphate of zinc (37° to 38° B.), equal to about 50 per cent. of $ZnSO_4 + 7H_2O$, by passing hydrogen-sulphide gas through it until it is saturated with the gas. As soon as the precipitate of ZnS has settled, the acid liquor is run off and used for extracting more zinc and thus neutralize the excess of acid. Any injurious elements that are at the same time introduced must be precipitated by means of metallic zinc. The neutral solution of zinc sulphate thus obtained is added to the tanks containing the zinc sulphide and is now ready for electrolysis.

The electrodes are of sheet lead, but as soon as a deposit of zinc from 1 to 1.5 millimeters is obtained on the cathodes it is stripped off, trimmed, and used as cathodes in place of the lead.

The solution must be kept well agitated in order to keep the ZnS in suspension, as the purity of the deposit depends on this condition. As the deposition of zinc continues, the proportion of free sulphuric acid in the electrolyte increases. This slowly decomposes the zinc sulphide, which must be renewed as needed.

When the amount of free sulphuric acid reaches a certain limit (9 to 9½ ounces per gallon) zinc can no longer be deposited satisfactorily and the solution must be replaced by neutral zinc sulphate.

Zinc deposited by this process is said to be extremely pure, analyses showing no impurities except a little ZnS.

60. The Siemens and Halske Process.—The process proposed by Siemens and Halske is very similar to their process for electrolytic treatment of copper ores. The sulphide ore is treated with a solution of ferric sulphate $Fe_2(SO_4)_3$ containing free sulphuric acid. The zinc sulphide ZnS is dissolved, forming the sulphate $ZnSO_4$, and at the same time the ferric sulphate is reduced to ferrous sulphate $FeSO_4$, according to the following equation:

$$ZnS + Fe_2(SO_4)_3 = ZnSO_4 + 2FeSO_4 + S$$

The solution of zinc sulphate and ferrous sulphate is transferred to the electrolytic tanks and electrolyzed. Zinc

is deposited at the cathode and sulphur trioxide SO_4 liberated at the anode. The SO_4 combines with the ferrous sulphate, converting it into ferric sulphate and giving a return of electric energy to the circuit.

The process is not successful, owing to the fact that the leaching solution does not attack the sulphide ore readily and consequently the percentage of extraction is low; moreover, it is impossible to deposit pure zinc from solutions containing iron.

Siemens and Halske have later taken out another patent with a view to preventing the formation of spongy zinc. They claim that by keeping up a violent agitation of the solution, preferably by blowing large quantities of air into it, the metal can be deposited in a reguline state. A large company was formed to work this process in Australia, but they have not yet got beyond the experimental stage.

61. Hoepfner's Process.—In this process, unlike those previously described, the zinc is in solution as a chloride. Hoepfner used revolving cathodes made in the form of disks and obtained on them dense deposits of zinc. Carbon anodes were used. Separate cells are provided for the electrodes and the whole apparatus is devised with a view to recovering the chlorine evolved at the anodes. This process has been used successfully in England and elsewhere principally for the chlorine obtained, the zinc being considered more as a by-product.

62. Ashcroft's Process.—Of all processes proposed for the treatment of lead-zinc sulphides, this one has attracted the widest attention. It gave great promise of success and an enormous sum of money was expended in establishing works in New South Wales. It has not up to the present time proved a success. On account of its prominence, it is of especial interest and the investigations done upon it have resulted in the accumulation of a large amount of valuable information. In outline, the process is as follows: The finely crushed and roasted ore is leached with a solution of ferric chloride or sulphate. Ferric sulphate $Fe_2(SO_4)_3$

was originally used. This reacted with the zinc oxide, forming zinc sulphate and precipitating ferric hydroxide, reaction taking place according to the equation

$$3ZnO + Fe_2(SO_4)_3 + 3H_2O = 3ZnSO_4 + 2Fe(OH)_3$$

The zinc solution is separated from the ore residue by means of filter presses and is delivered to the electrolytic tanks. These tanks are built with canvas cells containing the anodes. Diffusion is prevented by having the level of the zinc solution a little higher than the level of the solution in the anode cells. The cathodes occupy the remaining space. The cathodes are of zinc. The anodes in the first two-thirds of the tanks are made of cast iron and in the remaining one-third of carbon. The zinc solution, purified and free from iron, flows to the cathode divisions where zinc is deposited; thence it flows to the anode cells containing the iron anodes. Here the anion SO_4, formed by the decomposition of the $ZnSO_4$, combines with the iron of the anodes, forming ferrous sulphate $FeSO_4$. From the iron anodes the solution flows to the cells containing the carbon or lead anodes, which are insoluble. Here the anion SO_4 oxidizes the ferrous sulphate to ferric sulphate, according to the equation

$$2FeSO_4 + SO_4 = Fe_2(SO_4)_3$$

This solution containing ferric sulphate is now ready to be used for leaching fresh ore. A great deal of difficulty was encountered with black and spongy deposits of zinc and also the problem of purification of the electrolyte proved a difficult one.

ALKALINE PROCESSES

63. It is a well-known fact that zinc oxide is soluble in solutions of alkaline hydroxides, and some experimentation has been done with a view to depositing zinc from such solutions. The amount of published work done along this line is, however, much less than on the acid process and its practical success has not as yet been fully demonstrated.

64. S. Cowper-Cole's Process.—This is only partly an alkaline process. The ore is roasted to the oxide and leached with dilute sulphuric acid and the zinc sulphate thus obtained is electrolyzed on revolving cathodes, the zinc being scraped off as they revolve. The residue from the leaching containing chiefly lead oxide is now digested with caustic soda and the lead that is dissolved may be either deposited electrolytically or precipitated as white lead to be used as a paint by the addition of carbon dioxide. The process is being worked in Cornwall, England.

65. Hoepfner has also a process in which the zinc is leached out with an alkaline solution. This is run into a cell containing a porous partition, the alkaline solution being on the cathode side and an alkaline chloride on the anode. In this way, besides depositing the zinc, chlorine is evolved and may be utilized for other purposes.

66. Burghardt has also patented the use of ammonia and ammonium carbonate for the extraction of zinc oxide, oil being floated on the surface of the solution to prevent the volatilization of the ammonia. This process is being tried at Manchester, England.

67. E. C. Ketchum roasts and leaches the ores with 25 per cent. caustic alkali, whereby zinc and lead oxides are dissolved. The lead is then deposited out at about 1.8 volts and afterwards the zinc at about 2.1. Works were erected in New England for the purpose of investigating this process.

68. In regard to electrolytic zinc processes in general, it is safe to be cautious in accepting the statements of promoters of new processes for electrolytic treatment of zinc ores. It is, however, quite probable that some good results will soon be had along this line, but there is still much to be learned. Speaking generally, although a thoroughly good process has not yet been obtained, the electrolytic extraction of zinc has approached so near success and offers such possibilities that it has been considered here somewhat in detail.

NICKEL

69. Introductory.—The electrolytic treatment of nickel can be divided into two main headings. (1) The direct extraction from the ore or matte. (2) The refining of fairly pure metal, mainly with the object of recovering any precious metals it may contain. Neither of these processes has made much headway, the former never having got beyond the experimental stage, while the latter is now worked successfully, but has only been established at one works in the United States, namely, the Balbach Smelting and Refining Company, of Newark, New Jersey. The subject is, however, deserving of especial attention, owing to the high price of nickel and the complexity of the present methods of treatment. It might at first seem probable that crude nickel could be treated after the manner of the electrolytic process for copper, but a consideration of the nature of the impurities with which nickel is usually found will show the impossibility of this. Nickel requires a high voltage for deposition, and at this voltage most of the impurities will be deposited with it, particularly iron.

70. Applications of Nickel.—Nickel is used considerably for domestic utensils, either pure or in the form of nickeled sheet iron. Many other objects in every-day use are made from alloys of nickel, while its use for nickel-plating baser metals with a view to protecting them and improving their appearance is too well known to require any further reference here. Mixed with copper, it is used largely for coinage and the manufacture of German silver. Alloyed with iron, it is valuable for armor plate and such purposes and is then spoken of as ferro nickel and nickel steel.

71. Treatment of Nickel Ores.—The most common source, in fact almost the only source in America, of nickel is pyrrhotite, which occurs more or less mixed with chalcopyrite, so that the impurities from which the nickel must

be separated are cobalt, copper, iron, and sulphur, with small quantities of platinum, gold, silver, palladium, and traces of other elements. Nickel cannot be deposited from acid solutions under normal conditions, but can be from the double sulphate of nickel and ammonium in a slightly alkaline solution. In fact, this solution is used extensively for electroplating. Owing, however, to the high voltage, it is necessary to free the solution from all other impurities to prevent their being deposited with it.

72. Andre's Process.—This was one of the earliest suggestions made for the electrolytic extraction of nickel. Andre proposed that nickel mattes, speiss, or impure nickel cobalt, and copper compounds should be connected to the positive pole of a generator and suspended as anodes in dilute sulphuric acid. Copper or carbon plates are used as cathodes to receive the deposit of pure copper, for the nickel passing into solution is not deposited as long as the electrolyte is acid. In order to separate every trace of copper from the solution, a carbon plate is substituted towards the end of the operation for the matte or alloy used as the positive pole. The copper is then deposited very rapidly by the current, so that there remains a weak acid solution of nickel sulphate containing a little iron. A small quantity of ammonia is then added to the solution and air is passed through it while it is being evaporated in leaden pans. The iron is thus separated as the flocculent hydroxide and is removed either by sedimentation or by filtration. Pure nickel sulphate could then be obtained from the solution by concentration. In order to recover metallic nickel from this solution, the iron is first removed in the manner indicated and then the nickel is deposited on carbon, nickel, or black-leaded copper anodes, the solution having first been made ammoniacal. By suspending the matte, speiss, or the like as anodes in an ammoniacal bath, copper or nickel is deposited simultaneously, and this alloy can be treated again after its removal from the carbon plates.

This process may be regarded as typical of all the nickel processes that have been from time to time suggested.

73. Basse and Selve claim that with an alkaline solution in the presence of tartaric acid, dextrose, or glycerin, nickel cannot be deposited, while the other metals can. In this way they propose to separate it, the nickel being afterwards electrodeposited when the solution has been carbonated.

74. Hoepfner's nickel process is similar to his copper process previously described, it being claimed that the cupric chloride will dissolve out the sulphide of nickel in the same way that it does the sulphide of copper.

75. Jules Strap, in his patent of 1891, uses a copper-nickel matte as anode in a solution of acidified copper sulphate and so deposits out all the copper, leaving the nickel sulphate in solution, from which it is recovered by suitable means.

76. Hans A. Frasch has taken out a patent for a process for the treatment of copper-nickel ores. The matte is ground, spread on a horizontal sheet, and used as the anode. The electrolyte is a solution of sodium chloride. In this way the matte is dissolved at the anode and caustic soda formed at the cathode. This process is to be tried on a large scale at Hamilton, Ontario, Canada.

77. Speaking generally, the electrolytic extraction of nickel direct from the ores or matte has not proved practical so far. The refining of nickel and the recovery of the precious metals has, however, met with better success.

ELECTROLYTIC REFINING OF NICKEL

78. Previous to the establishment of nickel refining at the Balbach Works, Newark, New Jersey, it had been found impossible to deposit nickel with any degree of facility, the nickel curling up and stripping off the plate as soon as it

reached any thickness. These strips were troublesome to collect and almost impossible to melt into ingots without serious loss. Cathodes $\frac{3}{8}$ inch thick, however, are now produced regularly at the Balbach Works. This electrodeposited metal is very tough and elastic and particularly difficult to chisel. It can be hammered and punched without cracking and is as troublesome to manipulate as tempered steel. It is now generally understood that this end is attained by keeping the electrolyte at a temperature of from 50° to 90° C. and thoroughly stirring it. The electrolyte consists of a solution of nickel sulphate kept neutral or slightly alkaline. The precious metals, consisting of platinum, palladium, gold, and silver, mostly fall to the bottom of the tank as mud. There is, however, very little separation of the iron and cobalt, nearly all of it being deposited with the nickel. This is what would be expected when it is remembered how similarly these three metals behave chemically.

79. Below is given the result of an experiment by Dr. Foerster to show what became of the impurities. The anode contained .40 per cent. of carbon C, .02 per cent. of silicon Si, .10 per cent. of copper Cu, .43 per cent. of iron Fe, .14 per cent. of cobalt Co, .02 per cent. of manganese Mn. Of these, the carbon, silicon, copper, and manganese were completely eliminated and no trace of them could be found in the cathode nickel. The iron and cobalt, however, were present in the refined metal in almost undiminished quantity. At the Balbach Works, the anodes give the following analysis: Nickel, 95 per cent.; copper, .55 per cent.; iron, .75 per cent.; silicon, .25 per cent.; carbon, .45 per cent.; sulphur, 3 per cent. (purposely added to facilitate the casting). The refined metal is exceptionally pure and does not contain more than .03 per cent. of arsenic and .02 per cent. of sulphur. The cathodes are about 20 in. × 30 in. in size. Of the precious metals recovered, the one of chief importance is platinum, which averages about 1 ounce per ton. There are also small quantities of gold, silver, and

palladium, the total value of precious metals being in the neighborhood of $30 per ton. One great objection to the process is the large amount of anode scrap that is produced, the anodes showing a great tendency to crumble and crack. The melting point of nickel is so high that the casting of anodes becomes a matter of considerable expense. The company is generally reluctant to reveal working details of their plant and process, but the main particulars have been given.

A SERIES

OF

QUESTIONS AND EXAMPLES

RELATING TO THE SUBJECTS

TREATED OF IN THIS VOLUME.

It will be noticed that the various Examination Questions that follow have been divided into sections to which have been assigned the same section numbers as the Instruction Papers to which they refer. No attempt should be made to answer any of the questions or to solve any of the examples until the Instruction Paper having the same section number as the section in which the questions or examples occur has been carefully studied.

HYPOSULPHITE LIXIVIATION

EXAMINATION QUESTIONS

(1) To lixiviate silver ores, what must first be done, provided the Russell process will not treat them ?

(2) What tests are to be made in order to ascertain whether an ore may be leached with a hyposulphite solution ?

(3) (*a*) When free iodine is added to a solution of starch, what characteristic color is produced ? (*b*) How are hyposulphite solutions tested ?

(4) How does the von Patera process differ from the Kiss process ?

(5) How does the Russell process differ from the Kiss and von Patera processes ?

(6) What steps are to be followed when using the von Patera or Kiss process ?

(7) When chloridizing roasting for hyposulphite lixiviation, what matters are to be guarded against ?

(8) What two distinct operations are involved in hyposulphite lixiviation ?

(9) What reaction occurs when silver chloride is dissolved by sodium hyposulphite ?

(10) How is the silver sulphide precipitated from the solution ?

(11) Describe the method of refining sulphide precipitates.

(12) Ores containing lead have that metal dissolved in considerable proportions if treated with calcium or sodium hyposulphite. How may the lead be precipitated without precipitating the other metals in the solution?

(13) What advantages has the Russell process over the von Patera process?

(14) What advantages are there in removing lead by separate precipitation?

(15) Describe the method of working ores that do not require roasting, such as tailings and free-milling ores.

(16) Describe a filter for the hyposulphite process.

(17) New mills should be started on a 2-per-cent. hyposulphite-of-sodium solution. State how you would make such a solution.

(18) State how to prepare the extra solution.

THE CHLORINATION PROCESS

EXAMINATION QUESTIONS

(1) Describe the essence of Plattner's process.

(2) What effect did Delacy's improvement have upon the process?

(3) What particular features were there in the Mears chlorination process?

(4) How did Theis improve on barrel chlorination?

(5) Upon what chemical reaction is the chlorination process based?

(6) What chemical reactions occurred when Plattner's method of generating chlorine gas was practiced?

(7) What chemical reactions occur when the Theis method of generating chlorine gas is practiced?

(8) What reaction took place when gold was precipitated by Plattner's method?

(9) (*a*) What effect does sulphur dioxide have upon the trichloride-of-gold solution? (*b*) What would be the effect if an excess of sulphur dioxide was added to a trichloride-of-gold solution?

(10) What reaction occurs when hydrogen sulphide is added to a trichloride-of-gold solution?

(11) State the cause for roasting ores dead.

(12) When is salt to be added to an ore and for what purpose?

(13) What object is there in oxidizing roasting?

(14) What object is there in roasting dead?

(15) Describe chloridizing roasting.

(16) What tests are generally made to determine whether an ore can be treated by the chlorination process?

(17) How will one test a chlorine solution for gold?

(18) What are the conditions necessary to successful chlorination?

(19) The floating siphon is employed as an appliance in many operations besides chlorination. Describe it and suggest in what other instances it may prove useful, if you know of any.

(20) What object was there in dampening and sifting ore into the Plattner vats?

(21) How could the millman determine when there was enough gas in the Plattner vat?

(22) What chemical was employed in the Plattner process for precipitating gold?

(23) For what purpose are pressure tanks used in the chlorination process?

(24) What is used to catch the precipitates in the filter press?

(25) Water is first put in the barrel and then acid. Explain, if you can, the reason for this.

(26) Should bleaching powder be left exposed to the air?

(27) Calculate the quantity of bleaching powder required when the capacity of the barrel is 240 cubic feet, the water 840 gallons, and the ore 86 cubic feet, the temperature for calculating purposes being 60° F. and the barometer 30 inches.

(28) When ore is not thoroughly oxidized, what effect has it upon the consumption of chemicals?

(29) How is it possible to determine the quantity of sulphuric acid needed for barrel chlorination?

(30) How much water is needed for the ore in a chlorinating barrel?

(31) (*a*) How long is a barrel revolved in the chlorination process? (*b*) Upon what does the time for leaching depend?

(32) By what means can the degree of extraction in the barrel be determined?

(33) What are done with the filter-press sulphide and the gold cakes?

(34) Why should a mold be heated before running in gold?

(35) Upon what ores may chlorination be practiced?

COPPER SMELTING AND REFINING

EXAMINATION QUESTIONS

(1) What ores of copper should be leached rather than smelted?

(2) What difference exists other than the shape of the furnace between blast and reverberatory smelting?

(3) When is a reverberatory furnace preferable to a blast furnace?

(4) What advantages do water-jacket furnaces have over brick?

(5) State the disadvantages of too much air blast.

(6) What is *matte?*

(7) What object is attained by roasting sulphide ores before smelting for matte?

(8) Why are the products of large furnaces allowed to escape almost as soon as they are formed?

(9) What effect does silica have upon smelting operations?

(10) What effect has iron upon smelting operations?

(11) What are the limits of silica, iron, and lime in slags?

(12) How much sulphur does a matte with 40 per cent. copper require?

(13) Why must care be observed when granulating slag?

(14) In a mixture containing 60 per cent. FeS, how much is iron and how much sulphur?

(15) What is considered the best fuel for matte smelting ?

(16) What is the usual air pressure for copper-matte-smelting furnaces to carry ?

(17) What will be the quantity of ferrous oxide that can be produced from 38.22 pounds of iron ?

(18) Why is pyritic smelting impracticable ?

(19) What character of furnaces is generally used for smelting black copper ?

(20) What kind of fluxes are used in reverberatory copper smelting ?

(21) Why are ingots dumped into water ?

(22) What effect has carbon monoxide upon the unfused material in the furnace ?

(23) What reactions occur when copper becomes oxidized in the Bessemerizing process ?

(24) Give the equation for the reduction of cuprous oxide to copper.

(25) What becomes of the ferric sulphate when copper is precipitated by scrap iron ?

(26) What is a regenerative hot-blast gas stove ?

(27) What is meant by Bessemerizing copper ?

(28) (*a*) What is blister copper ? (*b*) How is it produced ?

(29) How is it possible to determine when the sulphur and iron have been oxidized in Bessemerizing ?

(30) Why will a converter increase in capacity ?

(31) What becomes of converter slag ?

(32) (*a*) What is coarse metal ? (*b*) How is white metal produced ?

(33) What is best selected copper ?

(34) What is understood by copper refining ?

(35) What object is attained by poling ?

(36) Show the reaction which occurs when iron is roasted with salt.

(37) How is silver recovered from the leaching of copper ?

LEAD SMELTING AND REFINING

(PART 1)

EXAMINATION QUESTIONS

(1) (*a*) What effect has litharge with silica? (*b*) How does litharge act when combined with lime?

(2) What compounds are sometimes found with litharge and oxides?

(3) State some of the properties of lead sulphide.

(4) In the blast furnace, what does sulphur combine with to form matte?

(5) Write the reaction which takes place between lead sulphide and calcium monoxide.

(6) Describe some of the properties of lead sulphate.

(7) When does a silver-lead alloy become eutectic?

(8) What effect has zinc upon lead?

(9) What two methods of lead extraction may be followed?

(10) What reactions permit reverberatory smelting of lead?

(11) What limits reverberatory lead smelting?

(12) What three reactions occur in lead blast smelting?

(13) (*a*) What is flue dust? (*b*) How is it disposed of?

(14) What ores are suitable for blast-furnace smelting and not reverberatory?

(15) How are sulphur ores treated previous to blast-furnace smelting ?

(16) When sufficient silica is not present in slag roasting, what is to be done in order to sinter the ore ?

(17) What features of blast-furnace smelting are desirable ?

(18) How may the capacity of a blast furnace be enlarged ?

(19) (*a*) Where is the zone of fusion located in a blast furnace ? (*b*) What is understood by a hot top ?

(20) How are cycloidal blowers usually connected with furnaces ?

(21) When will Arents siphon tap fail to be successful ?

(22) What is the lowest percentage of lead that may be retained in ore ?

(23) How do ore purchasers settle for silica and iron in lead ores ?

LEAD SMELTING AND REFINING

(PART 2)

EXAMINATION QUESTIONS

(1) In your own language, describe the process of furnace work called blowing out.

(2) What dangers arise from allowing molten slag to run directly into a stream of water?

(3) How is slag usually removed and disposed of?

(4) Upon what does the fusibility of a slag depend?

(5) What object has the modern furnaceman in using as little iron oxide and as much silica as will comport with the proper running of the furnace?

(6) What are the practical limits of the three principal components of slag?

(7) Why are dolomites to be avoided for blast-furnace fluxes?

(8) When it is necessary to run slag high in zinc, what is to be done?

(9) When does matte appear in lead smelting?

(10) When will speiss appear in lead smelting?

(11) What advantage has hand roasting over mechanical roasting?

(12) What is the object of briqueting machines?

(13) What is the most desirable fuel to employ for lead smelting?

(14) What effect has too much blast upon a furnace?

(15) What is the object of a forehearth?

(16) Does all the matte settle in the forehearth?

(17) How does Bartlett's process deal with zinc-lead ores?

(18) Upon what theory is the desilverization of base bullion containing lead carried on?

(19) Describe in a few words how the Pattinson process is carried out.

(20) Describe in a few words Luce and Rozan's modification to the Pattinson process.

(21) What is the principle upon which Parkes process is founded?

(22) What is meant by the term softening base bullion?

(23) What is the object of zincing?

(24) What is done usually with the second crust?

(25) How is the distillation of zinc from the crusts accomplished?

(26) What becomes of the dross from the desilverization process?

(27) How does cupellation on a commercial scale differ from that in the assay office?

(28) How is doré bullion parted on a commercial scale?

ZINC SMELTING AND REFINING

EXAMINATION QUESTIONS

(1) What are the principal ores of zinc?

(2) Why is it difficult to smelt lead and zinc together?

(3) How does Bartlett obtain oxide of zinc?

(4) How can zinc be recovered from its ores on a commercial scale?

(5) Of what material are zinc retorts to be made?

(6) Describe why it is difficult to leach zinc ores.

(7) How is the Converse process conducted and what products are obtained?

(8) In the treatment of franklinite, what steps are now taken to obtain a marketable zinc?

(9) Describe the theory and principal obstacles to be overcome in zinc distillation.

(10) Why are machine-constructed zinc retorts more durable than hand-made retorts?

(11) (*a*) For what purpose and how are adapters used? (*b*) Of what material are adapters constructed?

(12) What particular care must be used in mixing ore charges and inserting them in the retorts?

(13) Why is not zinc carbonate charged directly into the retorts, the same as zinc oxide or silicate?

(14) (*a*) What are regenerative hot-blast stoves? (*b*) How do such stoves economize in zinc distillation?

(15) What are the chief impurities in zinc?

(16) When there is a mixture of lead, zinc, and iron in the well of a zinc-refining furnace, how does it feel to the touch when an iron rod is inserted?

(17) What effect do iron and lead have upon zinc which require their elimination before the zinc is marketed?

(18) (*a*) Into what product is the greater part of the zinc ore mined in the United States converted? (*b*) What use is made of this product?

(19) What becomes of the impure zinc skimmings obtained when refining zinc?

(20) State (*a*) the time required for distillation of zinc; (*b*) the quantities of coal required per ton of zinc extracted by Belgian and Silesian methods.

(21) (*a*) What is the percentage of recovery by zinc distillation? (*b*) What causes are responsible for losses during zinc distillation?

ELECTROMETALLURGY

(PART 1)

EXAMINATION QUESTIONS

(1) Describe static electricity.

(2) How may current electricity be generated?

(3) State the difference between conductors and non-conductors of electricity.

(4) Define electrical resistance.

(5) Whenever there is a difference of potential, in which direction will the current flow?

(6) Are electrodes capable of producing the same difference of potential when formed into a voltaic couple?

(7) If an electric circuit is broken by a conductor coming in contact with the conductors in the circuit, what will occur?

(8) State the difference between internal and external circuits.

(9) Describe the difference between multiple and series arcs.

(10) What three electrical factors are there in every electrical circuit?

(11) What is an ampere?

(12) The current from a voltaic cell decomposes water at the rate of 1.625 grains per hour; what will be the

strength of the current in amperes to decompose 7.27 grams of water per hour?

(13) Find the quantity of electricity that will flow around a circuit in 1 hour when the strength of the current is 21.6 amperes.

(14) Does the area of a conductor influence its resistance and if so, in what ratio?

(15) (*a*) What is a microhm? (*b*) Does heat influence the resistance of a conductor?

(16) In liquids, how may the resistance be decreased?

(17) Define a volt.

(18) What current can be made to flow through a circuit having a resistance of 15 ohms, if the E. M. F. is 250 volts?

(19) What voltage is required to send a current of 12 amperes through a resistance of 10 ohms?

(20) What analogy is there between a drop of potential and a loss of head in water flowing from a tank?

(21) Give the rule for joint conductivity when two separate conductors have equal resistances.

(22) How may the differences of potential in the branches of a derived circuit be determined?

(23) (*a*) What is a joule? (*b*) What is the unit of electrical power termed?

(24) What is an electrical horsepower?

(25) Describe the kilowatt.

(26) When electrolysis occurs, what gas is usually evolved at the cathode?

(27) Describe electrolysis.

(28) What relation exists between the metal deposited and the current in amperes?

(29) What are electrolytes and electrodes?

(30) What are ions, anions, and cations?

(31) Explain polarization.

(32) On what does the separation of metals by electrolysis depend ?

(33) What are secondary reactions in electrolysis ?

(34) Define the term dissociation as applied to electrolytes.

(35) Solutions of those salts which are completely dissociated are the best conductors; explain the reasons for this phenomenon.

(36) What is an electrochemical equivalent of a metal ?

ELECTROMETALLURGY

(PART 2)

EXAMINATION QUESTIONS

(1) What is the object in electrolytic refining?

(2) Describe the multiple system of electrolytic copper refining and state in what manner it differs from the series system.

(3) What are the bad features to the Smith process?

(4) How does the Randolph process differ from the Smith process with reference to the current and position of the electrodes?

(5) Which is the more efficient system, the multiple or series; and what is your reason for considering it so?

(6) Why should engines and dynamos for an electrolytic plant be carefully chosen?

(7) Describe the uses of the ammeter and voltmeter in electrolysis.

(8) How are tanks that are to contain the electrolyte for the multiple system lined?

(9) How are the overflow pipes from series tanks insulated?

(10) How are anodes made for electrolytic refining?

(11) How are cathodes made and with what are they covered?

(12) For what purpose are cross-conductors?

(13) What object is attained by keeping the electrolyte flowing from one tank to another?

(14) How are connections with anodes and cathodes made?

(15) When current density is doubled in an electrolytic refinery, what may be saved and what lost?

(16) (*a*) Why should electrodes be quite close together? (*b*) What regulates the distance between electrodes in an electrolytic bath?

(17) (*a*) What is meant by sprouting? (*b*) What is the cause of sprouting? (*c*) Where is sprouting most likely to occur?

(18) What is the voltage usually necessary to deposit copper?

(19) What chemicals must be tested for daily in order to obtain pure copper deposits?

(20) Why should an electrolyte be kept at a temperature of 70° F.?

(21) What becomes of the impurities of anodes?

(22) How does arsenic from anodes behave in the electrolyte when copper is being deposited?

(23) With a high current density, is deposited copper as likely to be impure as when there is an electrolyte weak in copper?

(24) What effect does tin have upon an electrolytic copper deposit?

(25) What becomes of the gold and silver in the copper anodes?

(26) What two methods are there for purifying the electrolyte?

(27) How is the copper obtained from the discarded electrolyte that has become too impure for use?

ELECTROMETALLURGY

(PART 3)

EXAMINATION QUESTIONS

(1) If anodes contain less than 30 ounces of silver, will it pay to refine them electrolytically? State the reason.

(2) On what does the current density required to refine a ton of copper depend?

(3) In designing an electrolytic refinery, what are the vital points to be studied?

(4) What is the distinction made between the refining and the extraction of copper?

(5) What are some of the hindrances to electrolytic refining?

(6) Name some of the advantages of the Hoepfner process of copper extraction.

(7) What does the electrolytic refining of doré bullion accomplish?

(8) In what form is silver deposited on the cathodes in the Moebius process?

(9) What electrolyte is used in the old Moebius process?

(10) Copper in dissolving requires three and one-half times as much nitric acid as silver; if, therefore, the copper increases in the electrolyte, what must be done?

(11) (*a*) How many grams of silver will a current of 22 amperes deposit in an hour? (*b*) What horsepower per hour will be required to deposit this amount, the voltage being .25?

(12) What mitigates against the theoretical deposit of silver in the Moebius process?

(13) How does the new differ from the old Moebius process?

(14) What two causes have been instrumental in opposing the electrolytic extraction of zinc?

(15) What two systems of leaching the ore have been tried?

(16) What was the first electrolytic process?

(17) Describe Ashcroft's process for zinc.

(18) (*a*) What is nickel used for? (*b*) From what is nickel derived?

(19) How is nickel refined electrolytically?

(20) Is the electrolytic extraction of nickel from ores a success?

A KEY

TO ALL THE

QUESTIONS AND EXAMPLES

CONTAINED IN THE

EXAMINATION QUESTIONS

INCLUDED IN THIS VOLUME.

The Keys that follow have been divided into sections corresponding to the Examination Questions to which they refer, and have been given corresponding section numbers. The answers and solutions have been numbered to correspond with the questions. When the answer to a question involves a repetition of statements given in the Instruction Paper, the reader has been referred to a numbered article, the reading of which will enable him to answer the question himself.

To be of the greatest benefit, the Keys should be used sparingly. They should be used much in the same manner as a pupil would go to a teacher for instruction with regard to answering some example he was unable to solve. If used in this manner, the Keys will be of great help and assistance to the student, and will be a source of encouragement to him in studying the various papers composing the Course.

HYPOSULPHITE LIXIVIATION

(1) Give them a chloridizing roasting. See Art. **1.**

(2) See Art. **3.**

(3) (*a*) Blue. See Art. **7.**

(*b*) Measure out hyposulphite solution, add starch, and titrate with a standard iodine solution, prepared as explained in Art. **8.**

(4) Kiss substituted calcium hyposulphite for the sodium hyposulphite of the von Patera process. See Art. **29.**

(5) Russell uses what is termed an extra solution of cuprous hyposulphite.

(6) See Art. **30.**

(7) Too much salt, fusing lead and forming lead silicates, loss of base metals. See Art. **31.**

(8) Leaching the base-metal salts with hot water and then the silver with hyposulphite solutions. See Art. **33.**

(9) See Art. **35.**

(10) See Arts. **38** and **39.**

(11) When silver is thrown down as sulphide, it is necessary to roast and drive off the sulphur preparatory to melting. See Art. **42.**

(12) By sodium carbonate prior to precipitating the other metals in solution. See Arts. **45** and **47.**

(13) Some of the advantages of the Russell process are that silver may be extracted in some cases without roasting the ore, and an additional quantity of silver may be extracted over the old method. See Art. **46.**

(14) Silver sulphide is freed from lead, lead is freed from base metals, saving of sodium sulphide. See Art. **50.**

(15) See Art. **54** and Chart, Fig. 3.

(16) See Arts. **58, 59,** and **60.**

(17) Use 125 pounds of sodium hyposulphite. See Art. **64.**

(18) See Arts. **65** and **69.**

THE CHLORINATION PROCESS

(1) The ore was placed in vats upon a false bottom, which served as part of a filter. The vats were made air-tight and chlorine gas was pumped in through a hole in the bottom. The gas gradually permeated the ore, and after several days water was added and the trichloride of gold $AuCl_3$ formed was leached out, the solution conveyed to precipitating tanks, and there thrown down as a brown powder by ferrous sulphate. See Art. **1.**

(2) It shortened the time required for chlorination. See Art. **2.**

(3) A lead-lined barrel was used, the ends of which were provided with hollow trunnions and goosenecks through which the gas was forced into the barrel under pressure. See Art. **3.**

(4) He introduced the method of generating the gas in the barrel, using for the purpose bleaching powder $2CaOCl_2$ and sulphuric acid H_2SO_4. These were placed inside the barrel with the ore. See Art. **4.**

(5) The solubility of gold in chlorine gas and the power that water has to dissolve the trichloride of gold. See Art. **6.**

(6) The manganese dioxide MnO_2, sodium chloride $NaCl$, and sulphuric acid H_2SO_4 generate chlorine gas. See Art. **7.**

(7) Bleaching powder $2CaOCl_2$ and sulphuric acid H_2SO_4 are used in this case to generate chlorine gas. See equation, Art. **8.**

(8) The gold was separated from the trichloride solution by means of ferrous sulphate $FeSO_4$ and thrown down as a brown powder. See formula, Art. **9.**

(9) (*a*) It drives off the excess of chlorine. See Art. **10.**

(*b*) Hydrochloric acid would be formed, the sulphur precipitated as a fine powder, and oxygen set free. See Art. **10.**

(10) The gold is precipitated as a yellowish-brown powder. See Art. **10.**

(11) The object is to get rid of the base metals that the chlorine would attack. See Art. **11.**

(12) When the ore contains lime, magnesia, or lead, salt is added near the end of the roasting to change these metals into chlorides. See Art. **11.**

(13) To convert the metals into oxides and sulphates. See Art. **12.**

(14) To remove the sulphates that would precipitate gold from the solution. See Art. **13.**

(15) The roasting is begun in the same manner as the oxidizing roasting, but at some time during the operation $NaCl$ is mixed with the ore, the quantity varying from 1 to 2 per cent. See Art. **14.**

(16) The ore should be assayed. A quantity of ore should be weighed, roasted dead, and reweighed. The gold should be extracted with chlorine. The tailings from the chloride solution should be washed, dried, and weighed. The gold should be precipitated and the precipitates refined. See Art. **16.**

(17) A little of the trichloride solution is placed in a test tube and a solution of sodium sulphide Na_2S added. The gold, if present, will be indicated by a dark-brown or black precipitate. See Art. **23.**

(18) The gold must be in a metallic state. The chlorine gas used must not contain hydrochloric acid. The ore must contain no substances that will unite with free chlorine. The gold must not be precipitated until the final solution has been drawn off. The gold and nothing else should be retained in the final solution. See Art. **24.**

(19) The floating siphon is a rubber hose having a wooden float attached at one end and a pipe fastened to the other. It may be used for any purpose where it is desired to draw off the clear liquid from a solution containing a sediment. See Art. **28.**

(20) To make a loose, porous mass that could be permeated by the chlorine gas. See Art. **30.**

(21) By testing for chlorine gas above the ore through a small hole in the cover of the vat. See Art. **32.**

(22) Ferrous sulphate $FeSO_4$. See Art. **34.**

(23) For precipitating and filtering. See Arts. **44-47.**

(24) Canton flannel. See Art. **47.**

(25) This is done to prevent an explosion, which might occur were the water poured on to the sulphuric acid.

(26) No. See Art. **50** for reasons.

(27) $\frac{840 \times 231}{1,728} = 112.3$ cubic feet of water.

$112.3 + 86 = 198.3$ cubic feet of space occupied by water and ore. .

$240 - 198.3 = 41.7$ cubic feet of space left in barrel.

$112.3 \times 2\frac{1}{3} = 262.033$ cubic feet of gas absorbed by water.

$262.03 + 41.7 = 303.73$ cubic feet of gas.

$w = \frac{1.3253 \times B}{459 + t} = \frac{1.3253 \times 30}{459 + 60} = .0766$, weight of 1 cubic foot of air under the above conditions.

$303.73 \times .0766 \times 2.45 = 57$ pounds of gas.

$57 \div .30 = 190$ lb. of bleaching powder. Ans. See Art. **51.**

(28) The metallic oxides absorb the chlorine. See Art. **52.**

(29) Determine the amount of chloride of lime required and remember that the relative amounts of chemicals used are 6 parts of bleaching powder to 7 parts of 66° B. commercial sulphuric acid. See Arts. **53, 54,** and **56.**

(30) The quantity of water usually required varies from 80 to 120 gallons per ton of ore. See Art. **54.**

(31) (*a*) The barrel is usually revolved from 3 to 6 hours, during which time tests are made for an excess of chlorine gas.

(*b*) The physical condition of the gold. See Art. **55.**

(32) By the gases issuing from a valve in the barrel. See Art. **56.**

(33) They are collected in an iron pan and placed in the muffle furnace, where the sulphur is volatilized. See Art. **65.**

(34) To avoid difficulty in removing the ingot when cold. See Art. **67.**

(35) It may be practiced on ores that contain impurities that are easily volatilized and have gold enough to warrant. Ores containing lime and magnesia cannot be treated and silver in ores is entirely lost. See Art. **69.**

COPPER SMELTING AND REFINING

(1) Certain low-grade ores. See Art. **4.**

(2) In the blast furnace, the ore is mixed with the fuel. In reverberatory smelting, the ore is kept separate from the fuel and is melted by hot gases from the fire. See Art. **5.**

(3) In smelting fine ore. See Arts. **11** and **12.**

(4) The walls are not corroded by the slags. See Art. **14.**

(5) First, fine ore would be blown out of the furnace; second, the intense heat generated would reduce considerable metallic iron, resulting in sows; third, the cold air might chill the fused material so that it would not run properly. See Art. **15.**

(6) An artificial copper sulphide. There are other mattes, for instance, lead, but copper is probably the only one for which smelting operations are carried on. See Art. **20.**

(7) To burn off the excess of sulphur. See Art. **22.**

(8) To prevent any unfused material from choking the furnace. See Art. **26.**

(9) It makes the smelting difficult. See Art. **27.**

(10) Iron is heavy, and a heavy slag will not separate well from the matte. Iron acts as a basic flux. See Art. **27.**

(11) Silica from 30 per cent. to 38 per cent., ferrous oxide and lime about 54 per cent. each. See Art. **28.**

(12) $128 : 32 = 40 : x$.

$x = \frac{32 \times 40}{128} = 10\%$. Ans. See Art. **30.**

(13) That there is plenty of water for the purpose and that no metal is run into the water to cause an explosion. See Art. **39.**

(14) Ferrous sulphide FeS has an atomic weight of 88 per cent. - 56 per cent. iron and 32 per cent. sulphur. $56 + 32 = 88$.

$$88 : 32 = 60 : x.$$

Then, $x = \frac{32 \times 60}{88}$, or practically 22 per cent. sulphur.

$60 - 22 = 38\%$ iron. Ans. See Art. **30.**

(15) Coke. See Art. **41.**

(16) From 8 to 12 ounces per square inch. See Art. **42.**

(17) The combining weight of iron is 56. The combining weight of oxygen is 16. $56 + 16 = 72$. $.16 \div .72 = 22$ per cent. oxygen.

$38.22 \times 1.22 = 46.71$ lb. FeO. Ans. See Art. **30.**

(18) Because pyrite will not keep up the heat without the use of other fuel. See Art. **51.**

(19) Blast furnaces. See Arts. **62** and **63.**

(20) Fluxes are not used. See Art. **69.**

(21) To give them a certain rose-red shade of color due to oxidation. See Art. **102.**

(22) It is a reducing agent and serves to separate the copper by the reactions. See Art. **110.**

(23) The sulphur is driven off in the form of sulphur dioxide. See Art. **89.**

(24) $2Cu_2O + Cu_2S = 6Cu + SO_2$. See Art. **91.**

(25) It is crystallized out of the solution and sold.

(26) An apparatus for heating the blast for a blast furnace. See Art. **58.**

(27) Oxidizing the sulphur and iron in a molten-copper matte by blowing a blast of air through it. See Art. **75.**

(28) Metallic copper having a blister-like surface. The copper dissolves a certain amount of sulphur dioxide while liquid, and the gas escapes when the metal cools, forming the blisters. See Art. **81.**

(29) By the colors of the smoke and flame, by the sound of the blast, and by the appearance of the solid particles blown out. See Art. **82.**

(30) The lining burns out. See Art. **83.**

(31) It is retreated in different ways. See Art. **84.**

(32) (*a*) A metal obtained by roasting the ore and then dissolving out some of the oxide of iron.

(*b*) By the Welsh method of copper smelting. See Art. **91.**

(33) A high grade of copper produced by retreating the white metal obtained by the fourth operation in the Welsh smelting process. See Art. **92.**

(34) Purifying the copper. See Art. **96.**

(35) The copper oxide is reduced to the metallic state. See Art. **99.**

(36) $Fe_2(SO_4)_3 + 6NaCl = Fe_2Cl_6 + 3Na_2SO_4$. See Art. **119.**

(37) The silver may be precipitated or it may be dissolved out of the solution as silver iodide. See Art. **123.**

LEAD SMELTING AND REFINING

(PART 1)

---

(1) (*a*) It unites with silica and forms a very corrosive lead silicate.

(*b*) With lime it combines and acts as an acid. See Art. **4.**

(2) Metallic compounds. Silver is found in the litharge of commerce, as stated in *Assaying*.

(3) It may be formed artificially. It may be fused at about the same temperature as litharge. It is rather volatile and very fluid when melted. It gives up its sulphur readily in the blast furnace. See Art. **6.**

(4) It will combine with copper to form matte.

(5) $4PbS + 4CaO = 3CaS + CaSO_4 + 4Pb.$ See Art. **8.**

(6) It occurs in nature. It is very stable and difficult to break up. See Art. **10.**

(7) When the proportions of the two metals are such that the alloy reaches its lowest fusing point. See Art. **18.**

(8) It injures lead for both mechanical and chemical purposes. See Art. **25.**

(9) Reverberatory- and blast-furnace smelting. It is impracticable at present to produce lead in the wet way. See Art. **29.**

(10) See Art. **9** and then Art. **10.**

(11) Lead smelting in reverberatory furnaces is limited to wet ores rich in lead. See Art. **30.**

(12) Reduction of lead by carbon monoxide derived from the fuel. The liberation of lead from silicates formed. The separation of the products formed by heat. See Art. **31.**

(13) (*a*) It is the condensed fumes from smelting operations, mixed with dust and carried into the flues by the mechanical action of the blast.

(*b*) It is collected from time to time and smelted.

(14) Dry ores or those low in lead and carrying considerable gold and silver. See Art. **57.**

(15) They are roasted to remove the sulphur. See Arts. **57, 58,** and **62.**

(16) Sand or quartz rock is added. See Art. **60.**

(17) The large output. Good fluid slag, which will not be pasty and which will tap well. See Art. **80.**

(18) By increasing its length rather than its width. The tendency of recent practice is to increase its height. See Art. **65.**

(19) (*a*) Just above the tuyeres.

(*b*) The zone of combustion working up so that melting occurs above the tuyeres. See Art. **66.**

(20) Blowers are usually connected with a single blast main. See Art. **77.**

(21) When the charge carries a considerable amount of copper. The reason for its not working then is stated in Art. **79.**

(22) From 6 to 7 per cent.; 5 per cent. is too low and is not usually paid for; above that limit it is paid for at the market price. See Art. **83.**

(23) The iron and silica are added together; if the silica exceeds the iron a charge is made for every unit in excess. See Art. **86.**

LEAD SMELTING AND REFINING

(PART 2)

(1) See Art. **4.**

(2) In case metal is in the slag, the steam generated will cause an explosion, and this scatters the slag and metal in all directions. Several persons have lost their eyesight in this manner. See Art. **10.**

(3) See Art. **10.**

(4) The fluxes used to produce the slag. See Art. **23.**

(5) Iron in the presence of lime tends to make a slag fusible; but iron ore costs more than limestone and frequently is difficult to obtain. Hence the smelter forces the slag as high in silica and as low in iron as may be consistent with good work. See Arts. **19, 22,** and **24.**

(6) Silica, 36 per cent.; lime, 30 per cent.; iron oxide, 52 per cent. are given as the highest limits. The lowest limits will be found in Art. **27.**

(7) Dolomites are basic, refractory substances. See Art. **32.**

(8) The iron must be increased or the lime decreased. See Art. **34.**

(9) See Art. **35.**

(10) See Art. **36.**

(11) The ore may be sintered into lumps, by hand roasters, and thus permit the furnace to work better. Ore may have its impurities removed more thoroughly. See Arts. **40** and **43.**

(12) Briqueting machines have a distinctive field at present among gold smelters. The field will probably be enlarged in time to iron furnaces. The object is to form lumps of ore from fine ore without sintering. See Arts. **40** and **43.**

(13) Coke which is not too pure. See Arts. **46, 47,** and **48.**

(14) It will drive the zone of combustion up into the furnace stack; it will cause hot top and also cool the hearth. See Arts. **49** and **50.**

(15) To separate slag from matte. See Art. **53.**

(16) No; not all. See Art. **54.**

(17) It converts the metal into oxides, which are then collected and worked into pigments. See Art. **69.** The Bartlett furnace is located at Cañon City, Colorado.

(18) Cupellation, by which means lead is oxidized into litharge. See Art. **73.**

(19) The Pattinson process depends upon silver having a different solidifying point from lead. The metal in excess will separate out first. This is taken advantage of, and the metal which crystallizes first carries crystals poorer in silver than the original metal. See Art. **75.**

(20) All the crystallizations are performed in one kettle by the assistance of steam. See Art. **79.**

(21) Upon the fact that zinc will not alloy to any extent with lead, while it will with silver, gold, and some other metals. See Art. **80.**

(22) Removing base metals. See Art. **81.**

(23) To remove the silver and gold. See Art. **84.**

(24) It is used for the first crust in the next zincing operation. See Art. **84.**

(25) By placing them in Faber du Faur furnaces, distilling the zinc, and condensing it. The silver remains in the furnace, also any gold present. See Arts. **94** to **97.**

(26) The dross is treated so as to separate its different metals. See Arts. **97** to **99.**

(27) In cupellation on a commercial scale the lead is converted into litharge. In laboratory cupellation the lead goes into the cupel and to waste. See Arts. **100** and **102.**

(28) Either with nitric or sulphuric acids, as explained in Art. **105** *et seq.*

ZINC SMELTING AND REFINING

(1) The principal ores of zinc in the United States are sphalerite in the Kansas-Missouri district; zinc silicate and zinc carbonate in Virginia; and franklinite in New Jersey.

(2) It is difficult to separate lead and zinc when in a metallic state. See Arts. **3** and **9.**

(3) By volatilizing the zinc in ores. See Arts. **11** and **12.**

(4) By retorting the zinc ores when mixed with carbon and then condensing the fumes to metallic zinc.

(5) Zinc retorts are made of fireclay or a mixture of green fireclay with old retorts ground up. See Art. **46.**

(6) The number of processes involved, hence the cost. See Arts. **19-21.**

(7) Concentrating and then magnetic separation. The products were zinc, zinc oxide, and spiegeleisen. See Arts. **31-33.**

(8) Magnetic concentration and jigging. See Art. **34.**

(9) *Theory:* Zinc oxide, zinc carbonate, or zinc silicate can be reduced to metallic zinc by incandescent carbon, and that metallic zinc is capable of distillation. *Obstacles:* Proper retort manufacture; impurities in the ore and fuel; condensation and loss. See Arts. **35, 38, 39,** and **41.**

(10) Machine-constructed retorts are formed under great pressure, and should therefore be less permeable to gases, and at the same time be strong from intimate mixture of the retort material. See Arts. **50** and **52.**

(11) (*a*) Adapters are placed upon the end of the retorts to condense the fumes of zinc.

(*b*) They are constructed of fireclay and broken retort material. See Art. **59.**

(12) The ore and coal should be thoroughly mixed and be uniform in size of particles. The coal should not be high in volatile hydrocarbons and there should be from $\frac{1}{3}$ to $\frac{2}{3}$ by weight as much coal as ore. See Art. **57.**

(13) There will be too much carbon dioxide in the retort unless the ore is calcined. See Art. **55.**

(14) (*a*) Regenerative hot-blast stoves are checkerwork of bricks. The bricks become heated by the hot gases escaping from the furnace to the stack.

(*b*) Such stoves save fuel by preheating the air entering to the furnace for combustion. See Art. **72.**

(15) The chief are lead and iron. See Art. **80** *et seq.*

(16) Like a cake of ice in water. See Art. **85.**

(17) Zinc containing iron is readily dissolved by acids. See Art. **80.** Zinc containing lead is not evenly attacked by acids and is tender. See Arts. **2** and **79.**

(18) (*a*) Zinc white. See Art. **88.**

(*b*) It is used as a pigment.

(19) They are added to the rich ore and returned to the retorts, or are sometimes liquated. See Art. **87.**

(20) (*a*) Usually about 24 hours. See Art. **76.**

(*b*) This varies, but possibly 4 tons on an average. See Art. **93.**

(21) (*a*) When 90 per cent. is recovered, it is considered excellent work, but more often it is much less. See Art. **38.**

(*b*) Loss from breakage of retorts; zinc retained in the ashes; escape of uncondensed zinc. See Art. **91.**

ELECTROMETALLURGY

(PART 1)

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(1) Static electricity resides as charges on the surface of non-conducting substances and is excited by various causes. See Art. **2.**

(2) By chemical action, by the action of heat, and by disturbances of the magnetic field, as in dynamos. See Art. **3.**

(3) Substances that resist the passage of electricity through them are called non-conductors. Substances through which electricity flows more or less freely are called conductors. See Art. **4.**

(4) A property of matter by which it *resists* the passage of electricity. See Art. **5.**

(5) From higher to lower potential. See Art. **9.**

(6) No. See Art. **12.**

(7) There will be a short circuit.

(8) The external circuit is that part of the circuit which is outside the electric source. The internal circuit is included within the electric source. See Art. **15.**

(9) When the positive electrodes are connected to one main positive conductor and the negative electrodes to one main negative conductor, the cells are said to be connected in multiple arc. A number of cells are said to be connected in series when they are arranged in one circuit by joining the

positive electrode of one cell to the negative electrode of the adjacent one. See Art. **17.**

(10) The electromotive force, the current, and the resistance. See Art. **18.**

(11) The practical unit of electric current. See Arts. **20** and **22.**

(12) 1 hour = 3,600 seconds. $C = \frac{W}{t \times .00009324}$.

$C = \frac{7.27}{3,600 \times .00009324} = 1.4$ amperes. Ans. See Art. **22.**

(13) $Q = Ct = 21.6 \times 3,600 = 77,760$ coulombs. Ans. See Art. **25.**

(14) The resistance of a conductor varies inversely as its sectional area. See Art. **32.**

(15) (*a*) One-millionth of an ohm. See Art. **39.**

(*b*) Yes; the resistance with metallic conductors increases as the temperature rises. See Art. **38.**

(16) By heat. See Art. **38.**

(17) The practical unit of electromotive force. See Art. **41.**

(18) $C = \frac{E}{R}$; $E = 250$; $R = 15$.

$C = \frac{250}{15} = 16\frac{2}{3}$ amperes. Ans. See Arts. **45** and **46.**

(19) $E = CR$; $C = 12$; $R = 10$.

$E = 12 \times 10 = 120$ volts. Ans. See Art. **46.**

(20) With water, there is a loss of pressure due to friction. With electricity, there is a loss of pressure due to electrical resistance of the conductor. See Art. **47.**

(21) If the separate resistances of two conductors are equal, their joint resistance when connected in parallel is one-half of their separate resistance. See Art. **54.**

(22) By multiplying the sum of the currents in the separate branches by their joint resistance in parallel. See Art. **56.**

(23) (*a*) The unit that measures the work performed in a given time.

(*b*) The watt. See Art. **58.**

(24) 746 watts. See Art. **61.**

(25) It is usually written K. W., and is equal to 1,000 watts. See Art. **62.**

(26) Hydrogen *H*. See Art. **66.**

(27) Electrolysis is the act of decomposing a solution by means of an electric current. See Art. **68.**

(28) The quantity of substance decomposed in a given time is proportional to the intensity of the current. See Arts. **67-69.**

(29) Electrolytes are the solutions undergoing electrolysis. Electrodes are the conductors that lead the current into and out of the electrolyte. See Art. **68.**

(30) Ions are the substances into which the liquid is decomposed. Anions are the elements liberated at the anodes. Cations are the elements liberated at the cathode. See Art. **68.**

(31) The various ions formed at the two electrodes adhere to or are absorbed by them and alter their electrical relations. See Art. **71.**

(32) On the electrochemical equivalent of the metal. See Art. **73.**

(33) The action of the liberated substances on the electrolytes. See Art. **78.**

(34) Dissociation means that the constituents of the molecules in electrolytes do not remain fixed, but are in a state of constant interchange. See Art. **87.**

(35) The conductivity of any solution depends on the number of free ions in it. See Art. **88.**

(36) The weight of that element brought into the ionic condition by 1 coulomb of electricity. See Art. **92.**

ELECTROMETALLURGY

(PART 2)

(1) To produce an exceptionally pure metal and to recover the gold, silver, platinum, and other valuable metals that may be alloyed with impure copper. See Art. **1.**

(2) In the multiple system the electrodes are alternately arranged, so that a positive anode will connect with a negative cathode. In the series system there is one anode and one cathode at each end of the tank; the current in this case passes through the electrode from one plate to the next until it leaves the bath. See Arts. **7** and **8.**

(3) Diaphragms give trouble. The slimes coat, giving them a certain amount of conductivity and increasing the danger of short-circuiting. The electrodes being in a horizontal position are not accessible to inspection, etc. See Art. **10.**

(4) The current flows in the opposite direction. In the Smith process, the anodes are arranged in series, horizontally. In the Randolph process, the anodes are placed one above the other with strips or blocks of non-conducting substance between. See Arts. **10** and **11.**

(5) The multiple system. There is a greater tendency for leakage to take place in the series system. See Art. **13.**

(6) Engines and dynamos must frequently run for 6 months at a stretch, and for this reason should be simple in design. See Art. **18.**

(7) The ammeter is used for the purpose of indicating whether deposition is going on at the required current density. It shows whether or not the dynamo is being overloaded, and by keeping a record of the average current the efficiency of the plant can be calculated from the amount of copper theoretically deposited by that current and the amount that is actually deposited. Voltmeters are used for indicating whether there are any short circuits or defective contacts in the tanks. See Art. **20.**

(8) With cement or asphalt. See Art. **23.**

(9) The pipes are made of some non-corrosive material, such as lead, with glass or rubber for insulating purposes. See Art. **23.**

(10) For the multiple process, they are cast directly from the converter, but for the series process they must be rolled. See Art. **25.**

(11) They are made by electrodeposition. Sheets of rolled copper, the surfaces of which have been oiled, are placed in tanks and the metal allowed to deposit upon them for 4 or 5 days, when they are removed and the metal stripped. They are usually coated with graphite grease and the edges dipped for about 1 inch in melted pitch. See Arts. **27** and **28.**

(12) To cross the current and hold the anode in place. See Art. **29.**

(13) A regular deposit and an even density of the electrolyte is insured. See Art. **30.**

(14) By means of strips of copper fastened to the upper side edges of the tank walls. The anodes and cathodes rest on these strips. See Art. **32.**

(15) There is a saving in first cost and in repairs, but the consumption of power is increased. See Arts. **37-38.**

(16) (*a*) The resistance of the electrolyte is thereby lessened.

(*b*) The parallelism between the plates. See Art. **40.**

(17) (*a*) The copper is said to "sprout" when it is deposited irregularly on the cathode and a portion of it is extended far enough to touch the anode.

(*b*) An uneven distribution of the current.

(*c*) At the edges of the cathode. See Art. **41.**

(18) This question is too indefinite, for which reason the following may be substituted: When the voltmeter reading is higher than usual, what is indicated?

ANSWER.—Dirty contacts, or that there is a thick layer of mud on the surface of the anode, or that the solution is getting weaker in free acid and is consequently of greater resistance, or that polarization is taking place. See Art. **71.**

(19) Copper sulphate $CuSO_4$; sulphuric acid H_2SO_4; copper Cu; silver Ag; and gold Au.

(20) To prevent crystallization. See Art. **43.**

(21) Some of the impurities are recovered as they fall to the bottom of the tanks. See Art. **59.**

(22) It dissolves and passes into the solution. See Art. **47.**

(23) The effect is the same in both cases, and impure copper will be deposited. See Arts. **47** and **48.**

(24) A beneficial effect. See Art. **51.**

(25) Both gold and silver go into the slimes unless the solution is neutral, when the silver may be deposited at the cathode. See Arts. **52** and **53.**

(26) In the one method, the impurities are precipitated. In the other method, a portion of the solution containing the impurities is drawn off and fresh solution added. See Arts. **56-60.**

(27) It is crystallized out as copper sulphate and formed into cement copper by contact with pig iron. See Art. **59.**

ELECTROMETALLURGY

(PART 3)

(1) No. The process is expensive and the price of the copper is very little higher than "best selected." See Art. **1.**

(2) The price of power, impurities in the copper, and interest on the capital. See Art. **6.**

(3) Output of copper desired, current density, voltage per tank, current per tank, number of tanks, number and size of electrodes, etc. See Art. **6.**

(4) By extraction is meant the recovery of copper from the ore. Refining means the purifying of copper. See Art. **10.**

(5) The chief hindrances are the cost of refining and the impurities in the copper.

(6) The copper being in a cuprous state requires but one-half the current for its deposition that it would in the cupric state.

The cuprous chloride combines with the chlorine at the anode and creates an electromotive force in a direction favorable to the process. See Art. **16.**

(7) The recovery of the gold and silver from the alloy. See Art. **18.**

(8) In coarse crystals of pure silver. See Arts. **24** and **42.**

(9) A weak solution of copper and silver nitrates, acidified with nitric acid. See Art. **26.**

(10) Nitric acid must be added more frequently. See Art. **26.**

(11) (*a*) 1.12 mg. × 22 × 3,600 = 88.684 grams. See Art. **37.**

(*b*) $\text{H.P.} = \frac{W}{746} = \frac{E\,C}{746} = \frac{22 \times 25}{746} = .74$ horsepower. Ans.

(12) The time consumed in cleaning up the gold and silver, examining insulations, etc., and the constant need of repairs. See Arts. **37** and **38.**

(13) In the form and arrangement of the electrodes and in the mechanical device used for removing the deposited silver from the tanks. See Art. **43.**

(14) The low price of zinc and the difficulty experienced in depositing it in a condition suitable for melting. See Art. **51.**

(15) Leaching with acid and alkali solutions. See Art. **53.**

(16) Luckow's process. See Art. **55.**

(17) The ore is leached with ferric sulphate and the zinc deposited from the zinc-sulphate solution by electrolysis. See Art. **62.**

(18) (*a*) For domestic utensils. See Art. **70.**

(*b*) Chiefly from pyrrhotite. See Art. **71.**

(19) The electrolyte consists of a solution of neutral or slightly alkaline nickel sulphate which is kept at a temperature of from 50° to 90° C. and thoroughly stirred. See Art. **78.**

(20) It is not considered so, although one refinery continues to work under a secret process. See Art. **77.**

INDEX.

NOTE.—All items in this index refer first to the section (see the Preface) and then to the page of the section. Thus, "Anglesite 36 6" means that anglesite will be found on page 6 of section 36.

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